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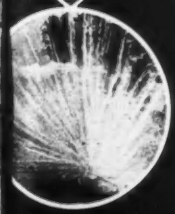

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Editorial:
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The Unexpected

▶ THE ONE generalization about members of the halogen family that is undeniably true for all is that they are gifted with strong individuality. We tend to think of chlorine as the type, because its compounds are the most familiar. But if anyone ever thought of fluorine as a sort of junior edition of chlorine, such an idea must show up more and more wide of the mark as the compounds of this lightest halogen become better known.

Fluorine enters into combination not only with the usual sorts of elements (sodium fluoride is a well-known insecticide) but with quite unexpected ones—oxygen, sulfur, phosphorus, arsenic, and even chlorine and the other halogens. With the usually mild boron it forms a very reactive radical, $-BF_4$. Fluorine makes silica vanish, yet it can be kept in iron. Its compound with silver is soluble, so the standard test for the halides does not reveal it. Possibly it occurs in minerals where this peculiarity has let it be overlooked. Fluorine's most poisonous compound, "1080," an Army top secret, occurs in a weed growing luxuriantly in South Africa.

One researcher reports a fluorine compound he tried to get into solution. The exasperating thing had to be refluxed with strong caustic for a week before it would do anything but just sit there in its own placid way. Another researcher tried to find the freezing point of another fluorine compound—an ordinarily safe enough procedure! and it not only blew up but every other bit of the material in the room exploded sympathetically.

Among fluorine's compounds are the most energetic, the least reactive, the safest, the most dangerous, the most toxic, the least harmful—in everything their qualities are superlative. As a field of research, fluorine is the newest, the strangest, the least predictable, the most exciting!

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Editors: WATSON DAVIS and HELEN MILES DAVIS

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➤ LIQUID *chlorine trifluoride poured onto wood produces this violent reaction. Many fluorine reactions with organic material are accompanied by flame.*

Flamboyant Fluorocarbons

by HELEN M. DAVIS

➤ "DOWN IN FLAMES", most spectacular of all the new horror deaths may become less of a hazard because of fluorocarbons. These new compounds are oily liquids and greasy solids whose properties make them seem promising as lubricants.

If they prove as useful for this purpose as chemists hope, we can get away from the necessity of lubricating engines with materials too dangerously like the fuel the engines burn.

Ours is by nature a hydrocarbon world. Hydrocarbons are related to fluorocarbons, but they have important differences in flammability. Petroleum and the many things made from it, as well as wood, paper and other plant products we use, including our food and clothing, are largely hydrocarbons.

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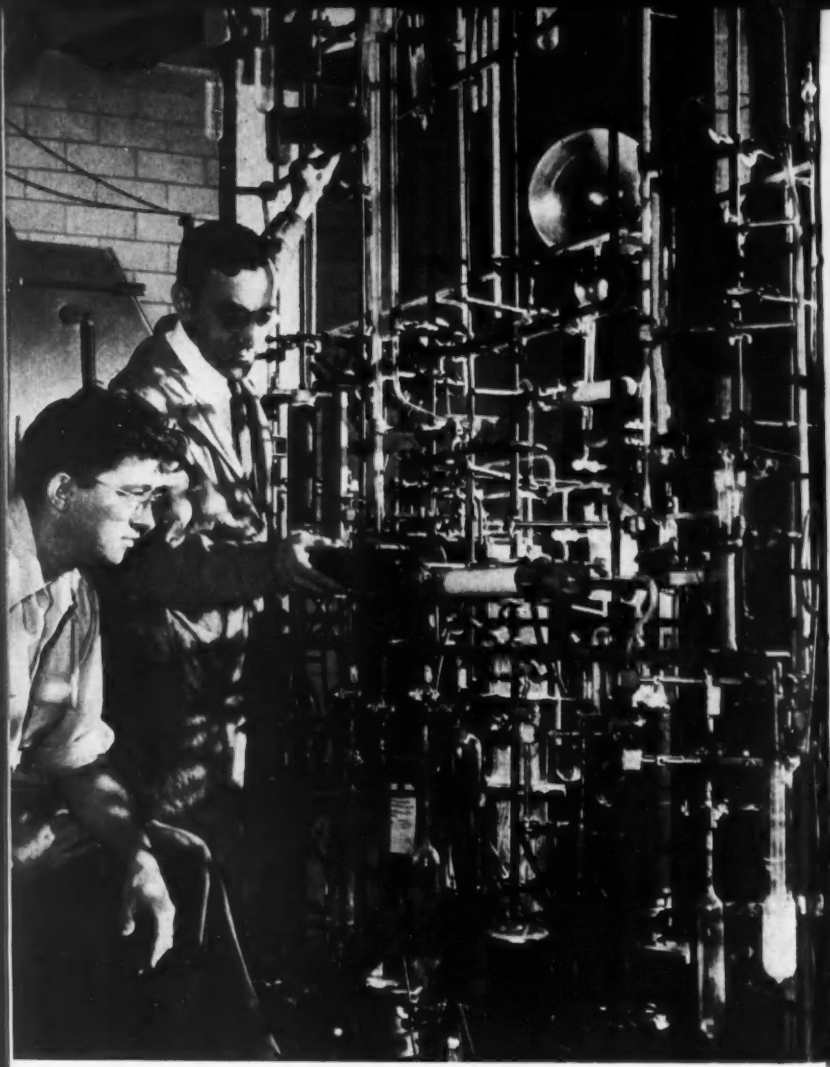
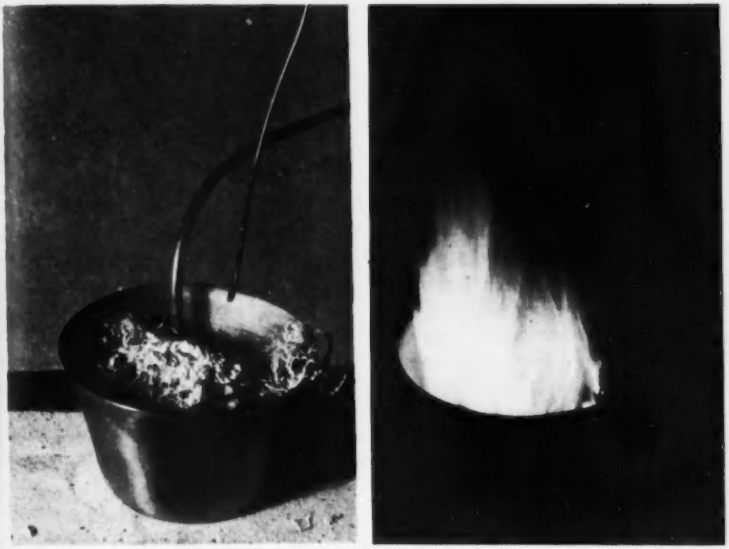


➤ IN THE *fluorine laboratories of The Pennsylvania State College, Dr. Joseph H. Simons, director of the laboratory, and Dr. Thomas J. Brice, of the staff, inspect the apparatus in which they handle derivatives of this unfamiliar element.*



SHAVINGS *of Teflon, the fluorine-containing plastic developed for use with fluorine compounds, do not burn in chlorine trifluoride if they are perfectly clean (left), but burst into flame (right) when a tiny speck of organic dust, picked up on the wire shown in the picture, is dropped onto them.*

Hydrocarbons burn in oxygen, and air is one-fifth oxygen. We live so closely with fire that we take it for granted. News of disasters is constantly recurring because somebody relaxed for an instant the guard we must all keep against letting uncontrolled fire get started.

Yet the chemist knows many materials that will not burn. It would seem sensible to use materials of that sort around hot engines where present-day greases often catch fire. The difficulty lies in the cost, for nature does not provide us with fluorocarbon oilwells.

But as the temperature of engines goes up, with the development of jet-propulsion, need for non-combustible materials is changing our viewpoint. We are reaching the place where we cannot afford the risk of flammable lubricants regardless of cost.

When a point like that is reached in any industry, the only economical way out of the dilemma is through fundamental research. Only when all the conditions the user and the manufacturer are likely to run into are thoroughly understood at the outset is it worth while to start a production program.

The United States Navy, which is one of the largest users of mechanical devices, finds itself interested in fundamental research problems in many fields. The properties of fluorocarbons and the problems of their manufacture were the subjects of a symposium held recently in Washington by the Chemistry Branch of the Office of Naval Research.

Here representatives of laboratories investigating fluorocarbon behavior and industries experimenting with fluorocarbon production exchanged information helpful to all who have to deal with the unfamiliar material.

Fluorocarbons are made, in general, by taking the hydrogen out of hydrocarbons and putting in fluorine in its place. Fluorine is one of the 96 chemical elements. It is a colorless gas, and is such an active one that it is never found loose in the atmosphere, as oxygen and nitrogen are. Most of it is locked up in a mineral called fluorspar.

Fluorspar is used as a flux in the metallurgy of steel. That is where the name comes from. Fluorspar makes the blast-furnace charge flow. Fluorine is the element from fluorspar.

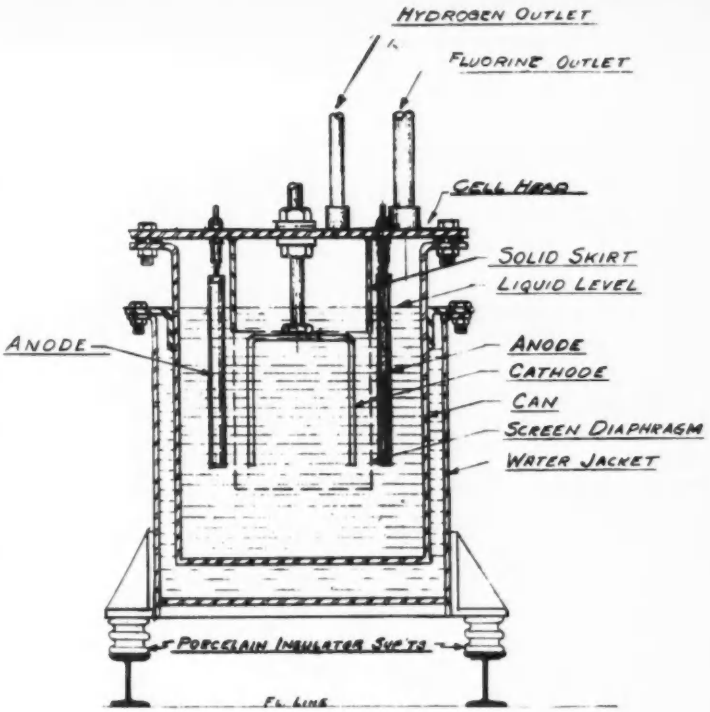
It is a dangerous and extremely unpleasant element to work with. Although it was discovered about 150 years ago, nothing much was done with it except etching glass until the fabulous research project that resulted in the atomic bomb got under way. Nearly everything about that project came straight out of the laboratory. The methods and materials used had never before been developed on an industrial scale.

Chemists of the atomic bomb project needed a compound of uranium which they could handle in the form of a gas. The slim chance of being able to separate the uranium isotopes depended on getting the material into the gaseous state. They searched the literature for reports of work on uranium compounds, most of which had resulted from sheer curiosity (and some of which, they found, were wrong). The only compound they found that would answer their purpose was the fluoride: UF_6. To get uranium into that form they had to provide for continuous production of fluorine. And fluorine is the element that corrodes practically everything and causes many metals to burst into flame.

Conditioned as we are to a world of carbon, oxygen and hydrogen, we interpret many experiences too narrowly in terms of these elements we know so well. Flame means burning, to us, and burning means carbon combining with oxygen. But flame can result from other combinations as well, where energy is given off in large amount.

Flame appears with many reactions of fluorine and its compounds. A stream of the element directed at a pan of water will make the water burst into flame. "Setting the river afire" could be a reality with this super-energetic material.

It might not seem, at first glance, that such a material would be promising for fireproof lubricants. But, turn to the other side of the picture. When a substance burns, it doesn't just "burn up". We think so because



—TYPICAL SECTION · CELL ASSEMBLY—

▶ DIAGRAM *showing construction of the fluorine cell pictured on the back cover.*

carbon, when it burns, forms a colorless gas that flies away. It seems natural to us that, by burning, a substance should disappear. But carbon burning in oxygen is a very special case. Nothing combines without forming a new material, and in most reactions the new mateiral, with its own ideosyncrasies, must be dealt with.

Many metals combine with fluorine to form gases that disappear. But when fluorine unites with compounds

of carbon, the material that is left is often a liquid or a solid. It is these compounds that interest lubrication engineers. Having already combined with the very energetic fluorine, the material that results is quite stable. To break up the fluorine compound would require more energy than the oxygen of the air could furnish. Therefore we call the fluorocarbon fireproof.

Fluorine is the lightest as well as the most active of a family of elements known to chemists as the halogens. In every chemical family there are family characteristics as well as individual differences. Knowing in a general way what the family characteristics are, chemists can predict with considerable accuracy how an unfamiliar element will behave and what its compounds will be like.

As soon as fluorine became commercially available, chemists were anxious to try making some of its compounds, to see whether they were the sort of stuff that had been predicted. In many ways the predictions were fulfilled, but the researchers got a good many surprises.

They expected fluorocarbons to be quiet and not very reactive. For compounds of the aliphatic series—straight chains of carbon atoms linked by single bonds—that is true. But when they tried combining fluorine with the aromatic hydrocarbons, they were surprised to find the reacting power of the resulting compounds increased.

Combinations of fluorine and chlorine in the same molecule often profoundly modify the properties of the hydrocarbon, beyond the effect of either halogen alone.

Fluorine and its compounds range from the greatest to the least in chemical activity, according to the statement of Dr. W. E. Hanford of the M. W. Kellogg Co., New York City, in summing up the Conference.

Among the deadliest poisons known can be classed the fluorine compound with acetic acid, the rat poison which is known as 1080. At the other end of the scale are freons and some other fluorocarbons with a toxicity of nearly zero.

Some fluorine compounds have melting points so low that only laboratories equipped to work with temperatures down near the absolute zero, where air is turned to ice, can measure them. Other materials made with fluorine are the highest melting plastics workable today.

Other properties of fluorine compounds that interest chemists are their high temperature stability and their low solubility in common solvents. They show low electrical losses, low refractive indexes and fairly high densities. These are the properties that indicate possible uses for these new materials.

Compounds of fluorine with carbon form a series of compounds, the fluorocarbons, which parallel in structure, properties and uses the familiar hydrocarbon compounds obtained from petroleum. In this series, compounds containing a single carbon atom include several related substances known as freons. These compounds, differing from each other in the proportion of fluorine to chlorine in the

molecule, are used in the cooling systems of modern refrigerators. They are used also in "bug bombs" to spray insecticides around as a fine mist.

Compounds of fluorine with two carbon atoms are used for much the same purpose as the freons, said Dr. Hanford. Chemists, he added, are trying to find uses for members of the series with three and four atoms of carbon.

Up in the range of 10 to 12 carbon atoms per molecule, the fluorocarbon compounds, like their hydrocarbon relatives, find uses as lubricants, greases and solvents. After this series, said Dr. Hanford, we take another jump to the higher molecular weight plastic materials.

Two of these, containing fluorine, are on the market today, the tetrafluoro-ethylene polymer and the trifluoro-vinyl chloride polymer. Resistance to corrosive chemicals and efficiency as electrical insulators are the important qualities of these materials.

Among the places that these plastics find use is in construction of apparatus for handling the element fluorine itself. The vinyl plastic can be made into thin-walled tubing that is practically transparent. This can be used for conveying fluorine, in place of the usual glass tubing, which is destroyed by the active element.

Present suplies of the mineral fluorspar, from which fluorine is obtained, were discussed by Dr. G. C. Finger of the Illinois State Geological Survey. Although the war played havoc with the fluorspar mines of Illinois and Kentucky, which are the leaders in domestic supply, Dr. Finger reported recent improvements in handling the mineral which should make the present visible supply last for at least 40 years. He called attention, however, to the possibility of obtaining fluorine from fluorophosphate deposits now worked for their phosphate content for fertilizer. The possibility of getting fluorspar from other parts of the world is also being explored by the Illinois Survey.

The conference on fluorides and fluorocarbons, sponsored by the Office of Naval Research, was organized by Dr. L. W. Butz and Dr. Ralph Roberts of the Chemistry Branch of the office. The opening session was addressed by Rear Admiral Thorvald V. Solberg, U.S.N., Chief of Naval Research.

Preparation of fluorides and fluorocarbons was the topic for discussion at the first session, under leadership of Dr. H. Cady, University of Washington, Seattle. At the afternoon session the same day Dr. Wm. T. Miller of Cornell University led discussion of the chemical properties of fluorides and fluorocarbons. The physical properties of these substances was the topic for the following morning, Dr. M. E. Hobbs of Duke University presiding. Dr. W. E. Hanford, of the M. W. Kellogg Co., led the discussion in the final session of the application of these fluorine compounds in industry.

Uses for fluorine and its compounds in dyes, in synthetic rubbers of the neoprene type, and in silicones were outlined by other speakers, among whom were Dr. L. A. Bigelow of Duke University, Dr. E. T. McBee of Purdue University, Dr. H. S. Booth

of Western Reserve University, Dr. Arthur Roe of the University of North Carolina, Dr. A. L. Henne of Ohio State University, Dr. Paul Tarrant of the University of Florida, Dr. R. H. Lafferty of the Carbide and Carbon Co., Oak Ridge, Tenn., Dr. K. E. Long of Harshaw Chemical Co., and Dr. J. R. Lacher of the University of Colorado.

Needs of the Navy for non-flammable lubricants, quenchers and hydraulic fluids were pointed out by Dr. W. A. Zisman of the Naval Research Laboratory.

Hydraulic fluids are commonly used in shock absorbers. The Navy makes much more extensive use of them in mechanisms of similar principle used to take up the recoil energy of big guns and to catapult planes from the decks of ships.

Quenchers are substances added to ordinary lubricating greases and oils with the expectation that, in case of fire, they will evolve non-flammable gases to smother the fire that generated them.

On the Back Cover

➤ FLUORINE *to the quantity of 150 pounds a day can be furnished by this cell which operates at 1500 amperes. A diagram showing its construction is shown on page 5. These illustrations and the photographs on pages 1 and 5 are from the Harshaw Chemical Co. which, since the end of the war, has made available two sizes of fluorine cells and a number of inorganic fluorinating agents to those interested in carrying out research in the field of organic fluorides.*

Detecting Flaws Inside Holes

➤ MAGNETIC iron oxide particles, fluorescent lights, a mirror and a surveyor's telescope are being used to detect tiny flaws on the inside surfaces of holes bored in long metal forgings. The process is a laboratory technique and is not for commercial uses.

This flaw-detecting method, in use in laboratories of the General Electric Company, can indicate flaws one five-hundredth of an inch wide in a boring 35 feet long. It involves magnetizing the forging and then blowing the iron oxide particles down the hole.

These particles align themselves with the north and south magnetic poles of any cracks or flaws which are present. Then a small cylinder on which three fluorescent tubes and a small mirror have been mounted is slowly drawn through the hole. A surveyor's telescope is used to view the mirror. Flaws in the forging, outlined by the particles, are visible.

Widely Occurring Active Element Yields Variety of New Compounds

Fluorine Chemicals in Industry

by G. C. Finger and F. H. Reed

This comprehensive account of fluorine compounds is taken from a report of the Illinois Geological Survey, on Fluorspar and Fluorine Chemicals. Within the state of Illinois and just across the state line in Kentucky lies one of the largest concentrations of fluorspar in the world. From these deposits, in great part, have come the fluorine resources that made Oak Ridge possible. Here experts in the winning of this unusual element for industry tell of its sources and applications.

➤ Fluorine is the most reactive element known to chemists in its free or elemental state. Consequently, it is always found in nature in the form of one of its compounds. It is widely distributed in the earth's crust to the extent of about 0.03 percent. This low percentage makes it appear that it might be a rare element. It is, to the contrary, three times as abundant as copper, fifteen times as abundant as lead, thirty times as abundant as cobalt, and two-thirds as abundant as chlorine. Just as the other elements mentioned are obtained commercially from minerals that contain a high percentage of them, so it is with fluorine. The chief fluorine-containing minerals of commercial significance are fluorapatite (rock phosphate), cryolite, and fluorspar. Fluorspar, also called fluorite, and known to the chemists as calcium fluoride, CaF_2, is the most important fluorine-containing mineral for the chemical industry.

There are several miscellaneous fluorine minerals such as amblygonite, $AlPO_4 \cdot LiF$, and lepidolite, $KLi[Al(OH,F)_2]Al(SiO_3)_3$ containing 13.5 and 9.5 percent of fluorine respectively. They are of no importance to the fluorine chemical industry, and are used solely in the ceramic industry or as a source of lithium.

Rock Phosphate

Fluorapatite, also called apatite or rock phosphate, has an approximate chemical composition of $CaFCa_4(PO_4)_3$ with a fluorine content of about 3.7 percent. It is a very common mineral and rather widely distributed throughout the world. Due to its wide distribution and the immense deposits, it can be considered to be the world's largest known fluorine reserve. Unfortunately the fluorine in fluorapatite is not readily available in a usable form for the chemical industry. On the other hand the rock phosphate industry merits attention. (1) The industry produces a certain class of fluorine-containing compounds known as the silicofluorides as by-products, and (2) this industry may serve as an alternate source of fluorine when the need arises. The silicofluorides are discussed in detail under the section on fluorine chemicals.

In order to appreciate the magnitude of the fluorine reserve in the rock phosphate deposits of the United States, a few simple calculations can be made. The inferred reserves of phosphate rock in 1943 were estimated to be approximately 11 billion tons. Assuming the fluorine content to be approximately 3 percent, the potential fluorine reserve is over 300 million tons and is equivalent to about 600 million tons of fluorspar. On the basis of a million ton world production of fluorspar in 1943, the phosphate rock reserves in the United States alone represent a world fluorspar reserve of approximately 600 years.

Cryolite

A naturally occurring mineral called cryolite, Na_3AlF_6, has the highest fluorine content of any known commercial mineral, 54 percent by weight. It is mined at only one place—Ivigtut, Greenland. The Danish government owns the mine and has a world monopoly. Its chief use is in the manufacture of metallic aluminum where the molten cryolite in the cells serves as a solvent for the alumina which is being electrolyzed. Other minor uses for cryolite are in the ceramic and insecticidal industries, and in some fluxing mixtures. Due to its cost and limited availability, it is not used as a raw material for a fluorine chemical industry. As a matter of fact, natural cryolite is seriously confronted with competition from synthetic cryolite prepared from fluorspar.

Fluorspar

The most important fluorine-containing mineral in industry today is fluorite, commonly called fluorspar, CaF_2. It contains 48.7 percent fluorine and 51.3 percent calcium, by weight, and is distributed widely in nature. In the United States, as pointed out in the section on economic aspects, the Illinois-Kentucky field accounts for 80 to 90 percent of the domestic production. The close proximity of this district, with its modern processing equipment, to industrial centers makes it the world's outstanding fluorspar area.

In general, fluorspar is associated chiefly with limestone and sandstone. Fluorspar associated with igneous rock of the quartz matrix type is the most difficult to process. Other minerals commonly found with it are galena, sphalerite, calcite, barite, etc. As the Illinois-Kentucky fluorspar generally occurs in beds of limestone or sandstone, it can be processed readily to a high-grade product unmatched in quality by a quartz matrix type. Generally, fluorspar is processed into metallurgical, acid, and ceramic grades. Almost all of the domestic spar is processed by some mechanical means. The modern installations use a heavy media and/or a flotation process, when a very high-grade product is desired. The flotation process enables the industry to recover such valuable by-products as lead and zinc ores which may run as high as 10 percent of the "as mined" product. The lead and zinc content varies considerably between mines, and in some places very little of the sulfide ore may be present. The heavy media process depends upon finely divided ferrosilicon to control the density of the slurry for efficient separation of the

fluorspar from its gangue material. A plant equipped with such a process has a very large production capacity, can handle readily an ore containing less than 40 percent CaF_2, and can produce a satisfactory metallurgical grade. As the heavy media process can be used economically on a low-grade ore, it is frequently used ahead of the flotation process to provide a much higher grade of feed for the flotation cells. In order to produce an acid or ceramic grade of fluorspar and at the same time recover the lead and zinc, a froth flotation is the standard process. This froth flotation process is unique in that it is the first continuous process devised to obtain two metallic minerals and a nonmetallic product all in the same operation. In the Illinois-Kentucky district most of the processing is done in the Illinois area.

Uses of Fluorspar

Metallurgical

The largest user of fluorspar is the steel industry. Approximately 60 percent of the fluorspar produced is of the metallurgical grade. It is used in the basic open hearth process as a flux to give fluidity to the slag, thus allowing the furnaces to be operated much more efficiently. In addition, it is of assistance in the removal of impurities such as sulfur and phosphorous. Depending upon economic conditions, the quantity of fluorspar used varies from one to fifty pounds per ton of steel with the average being five to eight pounds. Where speed and a maximum production are at stake, amounts higher than the above are used. A smaller amount of fluorspar is consumed in the electric-furnace steel, Bessemer steel, ferro-alloys, and iron foundry industries.

Chemical

Since 1936 the chemical industry has not only established itself as the second largest consumer of fluorspar, but has had a profound effect upon the technical development of the fluorspar industry in general. When the chemical industry increased its acid spar consumption from 20,000 tons in 1936 to a phenomenal demand of 129,000 tons in 1944, the fluorspar industry realized that here was an almost ideal type of customer from the standpoint of economic stability. Fortunately, the Illinois-Kentucky fluorspar interests met this challenge in a most positive way by installing suitable equipment and thus becoming the world's outstanding producers and processors of high quality acid spar. Circumstances are such now that the chemical industry need not hesitate to base its developments on a uniform and constant quality of raw material.

The chemical industry requires a high quality fluorspar with a maximum calcium fluoride content and a minimum of silica and calcite. This grade is known as acid spar and, as the name implies, is used in the manufacture of hydrofluoric acid.

Fluorspar or calcium fluoride is quite inert chemically and so is not used directly in many chemical operations. The chemical industry circumvents this difficulty by treating the

acid spar with sulfuric acid to form hydrofluoric acid. This acid has many desirable features: (1) By weight it contains 95 percent fluorine; (2) its fluorine is readily available for many chemical reactions; and (3) it is a very useful chemical in many non-fluorinating types of reactions. The summation of these features is reflected in the fact that hydrofluoric acid is now considered a major industrial chemical. Due to the fact that hydrofluoric acid is used, directly or indirectly, in almost every fluorine chemical process, it can be called the "key chemical." This is further verified by the fact that the production trends of hydrofluoric acid accurately portray the activities of industry in fluorine chemicals.

Outside of the manufacture of hydrofluoric acid, fluorspar is used directly in very few chemical reactions for reasons stated previously. Recently a new process has been announced for "winning the fluoride values from fluorspar" which avoids the usual hydrofluoric acid route. In brief, the process involves the interaction of fluorspar, sulfuric acid and boric acid in an aqueous medium to form fluoboric acid (HBF_4). A low-grade of fluorspar may be used. The fluoboric acid can be used as such or converted to fluoborate salts, or used in the production of synthetic cryolite.

Ceramic

The ceramic industry is the third largest user of fluorspar. A high quality product is required as indicated by the specifications under the ceramic grade. It is essential that the product not only have a high calcium fluoride content, but should be relatively free from iron or other coloring material. It is used in glass manufacture where opaque, colored, and clear glass is desired. Manufacturers of enamel and vitrolite use it as a fluxing and opacifying agent. The separation of the fluorides as solid crystallites is probably the important factor in opacity.

Miscellaneous

The miscellaneous uses of fluorspar are rather numerous. A small amount of fluorspar is used in the electrolytic cells in the manufacture of aluminum. The magnesium industry requires a small amount to satisfy its special needs. It is used in the manufacture of calcium carbide and cyanamide to facilitate the fusion and contact of ingredients. Occasionally some is used in the clinkering process for the manufacture of cement, and the rock wool industry in certain instances requires a small amount to reduce the viscosity of its rock melts. It is used as a paint pigment, as a binder in abrasives, as a mineralizer in certain ceramic operations, in the manufacture of carbon electrodes, as a catalyst, welding fluxes and rods, and in heat resistant brick. Since a very small amount of fluorine prevents dental caries, some new dentifrices contain a small amount of fluorspar. It is reported that 1-3 parts per million of fluorine in drinking water is sufficient to prevent dental caries; larger amounts are undesirable due to the possibility of causing a condition called mottled teeth. Some of the colored material has been used in inexpensive jewelry and stone ornaments.

A clear and colorless fluorspar called optical spar is used in various optical instruments because (1) it has a low index of refraction, (2) it has a high transmissibility to light, especially to ultra-violet, and (3) it displays no double refraction. Due to the great scarcity of natural optical material, a process for the production of synthetic crystals of fluorspar has been developed. The process involves the very carefully controlled cooling of molten calcium fluoride so as to produce a large single crystal. This development of growing synthetic crystals has revolutionized the optical instrument field due to the ready availability of crystal types and sizes.

Major Fluorine Chemicals in Industry

Any attempt to compile an extensive list of fluorine chemicals in the order of their relative economic importance would be almost impossible. The reason for such a situation is the lack of statistical information, and the reluctance of manufacturers to release production figures for competitive reasons. However, a few isolated facts stand out from which deductions can be made as to the major fluorine chemicals. Approximately 90,000 tons of acid spar valued at $3,500,000 was shipped from the mines for the manufacture of hydrofluoric acid and derivatives in 1947. The production of anhydrous and technical hydrofluoric acid for the same year was about 27,000 tons. As early as 1944, plant construction facilities were underway to achieve a monthly production of 2,400 tons of Freon. Turning to the silicofluorides, the Manufacturing Chemists Association reported a domestic production of more than 10,000 tons of sodium silicofluoride in 1944. These facts not only speak for themselves as to the stature of certain fluorides, but also give the market analysts an opportunity to speculate on the value of the entire fluoride industry. For the purposes of our discussion, the major fluorine chemicals will be listed as hydrofluoric acid, organic fluorides (the Freons), silicofluorides, synthetic cryolite, and aluminum fluoride.

Hydrofluoric Acid

The largest production of any fluorine chemical is represented by hydrofluoric acid. This acid is one of the most unique chemicals in industry for two reasons, (1) it is a "key chemical" in almost all fluorine chemical processes, and (2) it finds extensive application in non-fluorinating processes as a catalyst, reaction medium, etc. Hydrofluoric acid production in 1944 reached its peak of 45,700 tons (calculated as 100 percent HF). This tonnage of acid on an anhydrous basis represents over 2,100 tank cars, 21.6-ton capacity, or a train more than 12 miles long. The relaxation of war demands caused a recession in hydrofluoric acid production to a low of 21,000 tons in 1946, but its recovery since then has been steady as indicated by a production of 3,000 tons in August 1948. All indications are that this is a steady recovery due to greater diversification of uses and the development of new products. Anhydrous

hydrofluoric acid of over 99 percent purity is available in carload lots at a current price of 16 to 16½ cents per pound.

Aqueous and Anhydrous Hydrofluoric Acid

Two types of hydrofluoric acid are commercially available, namely aqueous acid and anhydrous. The difference is that the aqueous acid is a water solution of hydrogen fluoride whereas the anhydrous product contains no water of solution. The anhydrous produce is known in the trade as HF or anhydrous HF (also AHF) or by the misnomer of anhydrous hydrofluoric acid. From a chemical standpoint, these two products exhibit marked differences in properties and may be considered as two different types of chemicals. Both are made by the same basic reaction, namely by the interaction of acid spar with sulfuric acid in suitably heated kilns:

$$CaF_2 + H_2SO_4 \rightarrow CaSO_4 + 2HF$$

The manufacture of aqueous acid preceded the production of the anhydrous product by many years. The hydrogen fluoride gases from the preceeding reaction are absorbed in water in suitable lead cooling and absorbing towers. By recycling the absorption liquors, various strengths of acid can be obtained. Occasionally certain strengths are redistilled to give a higher quality acid. The usual strengths are 30, 40, 48, 52, and 60 percent; other strengths are available upon contract specifications. Those acids below 60 percent are generally shipped in lead or hard rubber containers, whereas 60 percent or higher may be handled in steel. More recently, the trend has been to dilute the anhydrous grade to the desired strengths. This arrangement is much more convenient as the anhydrous product can be stored in steel.

Anhydrous acid is made by the same general reaction, but under more rigidly controlled conditions. The retort is a large revolving steel kiln which is heated at 300-800°C. Finely ground acid spar is mixed with a slight excess of sulfuric acid in a hopper and then fed into the kiln. A large vent pipe serves as a collector for the HF and other gaseous products. At the far end of the kiln, the by-product calcium sulfate is usually expelled by a screw drive into water. The vent gases are passed countercurrently into sulfuric acid absorption towers. Some of the HF, some water, and most of the SO_2 and SO_3 are absorbed in the sulfuric acid. The sulfuric acid builds up in HF content, and the HF is recovered by heating. Both the recovered and the unabsorbed HF are combined and distilled through suitable columns. Besides the anhydrous HF (b.p. 19°C.) which is condensed to a liquid by a refrigerating system, an aqueous residue is obtained also. The SiF_4 formed from the silica present in the fluorspar passes through the entire system as a gas. The aqueous residue is fortified with sulfuric acid and returned to the scrubbing towers.

The silicon tetrafluoride gas (SiF_4) is passed into water absorption towers to form fluosilicic acid (H_2SiF_6). It is because of this by-product that hydrofluoric acid manufacturers prefer a low silica fluorspar as it mini-

mizes the loss of available fluorine. The fluosilicic acid derived from this source is channeled into industry in the same manner as the by-product acid derived from phosphate fertilizer plants.

Formerly, the type of equipment and the handling of hydrofluoric acid or its anhydrous product was of serious concern to the industry. Remarkable strides have been made in handling such a corrosive product so that all the operations are now within the realm of engineering materials well known to the chemical industry. Concentrations of acid above 60 percent can be conveniently handled in iron as well as magnesium, copper, monel, nickel, and brass. Lower acid strengths find lead a suitable engineering material; bakelite, wax, hard rubber, various plastics, such as polyethylene, are used also for container fabrication.

Uses of Hydrofluoric Acid

The uses of aqueous and anhydrous acid are many, and it is difficult to determine the consumption, value, and all of the specific uses for each type of acid. The Bureau of Census, Chemicals Unit, reports the production of the acid on a 100 percent HF basis and does not differentiate between the types of acid. In 1944 about 50 percent (24,900 tons) of the total acid production (45,700 tons as 100 percent HF) was earmarked as anhydrous acid. Indications as of 1948 are such that more anhydrous acid is being generated than aqueous. This agrees with the fact that the industrial trend is toward the anhydrous acid with subsequent dilution to the desired aqueous strengths.

Large tonnages of anhydrous hydrofluoric acid are used in the production of "alkylate" for the manufacture of 100-octane aviation gasoline and the Freon refrigerants. These items together account for the major consumption of the anhydrous product. The manufacture of the refrigerants is discussed below. Due to the development of HF-alkylation process by Universal Oil Products in 1942, the wartime demand for HF was very large. The HF functions as a catalyst for the conversion of olefines and isoparaffins into an "alkylate" that consists of a mixture of isomers of heptane, octane, etc. Unconfirmed reports indicate that some reactors use 50 tons of HF. Because the process is catalytic, very little "make-up" HF is needed to maintain the reactors at their capacity.

As the properties of anhydrous hydrofluoric acid or pure hydrogen fluoride (HF) are quite different from those of the aqueous acid, a brief resume of its outstanding properties will help to explain its unusual applications. It is a clear colorless liquid that freezes at —83° and boils at 19.5°C. Because its boiling point is close to room temperature, it can be handled either as a liquid or as a gas, and in many instances can be readily recovered from a reaction mixture. In the liquid state its density is about the same as water, and it is very hygroscopic which makes it fume in moist air and react vigorously with water or ice; it has a high dielectric constant, its surface tension is extremely low, and it has a high fluidity. Complete details on the properties of

this acid and materials of construction for handling are available in a number of publications and trade bulletins.

Anhydrous hydrofluoric acid is used in the preparation of inorganic fluorides, especially those compounds which are unstable in water solution, in the production of elemental fluorine, as the basis for a new electrochemical process for the direct synthesis of organic fluorocarbons, as a stripping agent for enamel coatings in salvaging steel from defective enamelware, and it is a suitable reaction medium for effecting nitration with sodium or potassium nitrate. Organic sulfonation reactions are performed also in hydrogen fluoride with a measure of success. Cellulose dissolves very rapidly in it to form glucose, and a wood sugar process developed in Germany depends upon this principle as a means of converting wood to sugar for fermentation to alcohol. Lignin can be recovered quantitatively from this process along with a certain amount of acetic acid.

The broadest field for the use of HF is in the organic chemical industry. This versatile material plays a dual role in organic syntheses: (1) It is used in the synthesis of organic fluorine compounds, and (2) it finds application in the synthesis of various types of nonfluorine-containing compounds. It can be used in such fields as fluorination, hydrofluorination, polymerization, esterification, catalysis, alkylation, reaction media, nitrations, sulfonations, diazotizations, molecular rearrangements, degradations, ring closures, etc. Some of these applications will be discussed later. The aqueous acid finds use in the manufacture of many inorganic fluorides and acid fluorides; frosting, etching, and polishing of glass; as an antiseptic in breweries and distilleries; electroplating; cleaning of copper and brass; in the making of filter paper and carbon electrodes; and for the removal of silica from graphite; also in the removal of efflorescence from stone and brick, extraction of tantalum and columbium, pickling and galvanizing metals. Occasionally hydrofluoric acid is used in acidizing oil wells to increase oil production.

In any discussion on the manufacture, handling, and uses of hydrofluoric acid attention must be called to the personal hazards involved. Both the liquid and vapors produce very serious and painful burns which heal very slowly if not properly treated. A bulletin, "The Treatment of Hydrofluoric Acid Burns," published by the National Institute of Health, Washington, D. C., covers the subject very thoroughly and every organization is strongly advised to obtain copies as a Safety First measure.

Organic Fluorides
The Freons

The phenomenal growth of the Freon refrigerants since their inception in 1930 to a proposed production capacity of 2,400 tons per month, as reported in 1944, represents one of the most outstanding developments in the synthetic organic chemical industry. Organic fluorine compounds prior to the advent of the Freons were considered laboratory curiosities, and the impact of these new refrigerants has

been the development of new types of fluorine-containing fumigators, plastics, dielectrics, dyes, solvents, lubricants, etc. In spite of their cost, these new products have found application where their unusual properties are unmatched by any other materials. Furthermore, these developments represent only "surface scratches" as to what can be expected in the future.

Most of these new developments trace their origin, directly or indirectly, to fundamental research by Swarts, a pioneer Belgian chemist. In 1892 he discovered a chemical reaction which enabled him to synthesize the Freons and many other compounds. In tribute to 40 years of pioneering research devoted exclusively to organic fluorine compounds, chemists have perpetuated his name in the Swarts reaction.

Refrigerants

In 1930, Midgley and Henne by means of the Swarts reaction announced the commercial production of a new group of refrigerants, called the Freons. The Swarts reaction, expressed in its simplest terms, involves the replacement of chlorine in a suitable organic chloride with fluorine by means of a metallic fluoride or anhydrous hydrofluoric acid. To illustrate the mechanics of this reaction, the synthesis of dichlorodifluoromethane (F-12), CCl_2F_2, is indicated by a chemical equation along with a description of the commercial process.

$$3\,CCl_4 + 2\,SbF_3 \xrightarrow{\text{catalyst}} 3\,CCl_2F_2 + 2\,SbCl_3$$

Into a heated autoclave or reactor containing antimony trifluoride and a catalyst both carbon tetrachloride and anhydrous hydrofluoric acid are fed continuously in a definite ratio. Antimony pentachloride is the catalyst most frequently used. The anhydrous hydrofluoric acid continuously regenerates the active fluorinating agent, antimony trifluoride. The reaction products pass into a distillation column where the free acids (HCl and HF) are separated from the Freon, and the insufficiently fluorinated raw material is returned to the reactor. For each chlorine atom that is replaced by a fluorine atom, there is a lowering of the boiling point by about 52° C., making the distillation operation very simple. The final product, after passing through scrubbing and drying towers, is condensed and shipped in steel cylinders, drums, and tank cars. By substituting carbon tetrachloride with other polychlorinated methanes and ethanes, various other Freons can be produced. It is obvious also from this discussion that these refrigerants are chlorofluoro derivatives of methane and ethane.

Since Freon is a family trade name, the various members are differentiated by code symbols for simplicity. F-12 is CCl_2F_2, the most common, and is loosely spoken of as Freon. Other members are F-11, CCl_3F; F-13, $CClF_3$; F-21, $CHCl_2F$; F-22, $CHClF_2$; F-113, CCl_2FCClF_2; and F-114, $CClF_2CClF_2$. In general, their outstanding features are stability, noninflamability, nontoxicity, and noncorrosiveness. They find extensive use in refrigeration and air conditioning equipment. The application and the type of compressor determines to a

great extent the choice of refrigerant. General Chemical Company in 1946 announced the availability of two fluorinated ethanes, CH_3CHF_2 and CH_3CClF_2, and called them "Genetrons" 100 and 101, respectively. A brief resume of the research on refrigerants in Germany appeared in a recent bulletin of the Office of Technical Services. In the chemical industry some of these compounds are used as intermediates in the manufacture of other fluorinated products. Certain fluorinated derivatives of propane and butane have been discussed in research circles as having practical application.

Aerosol Fumigators

An interesting application for F-11 and F-12 came as a result of the development of the aerosol fumigator or "bug bomb." The extermination of mosquitoes, flies, and other disease carrying insects in enclosed places became a matter of minutes with these fumigators. Briefly, the fumigator is a small, hand-sized cylinder filled with an insecticide, oil and Freon mixture, capable of fumigating a space of 150,000 cu. ft. When the ejection valve is opened, the Freon begins to boil, thus discharging the contents as a very fine mist which remains suspended in air for a long period of time. These fumigators were first delivered to the Armed Services in huge quantities and are available now as a household item. By far the largest percentage of Freon that is produced is consumed as a refrigerant and as a propellant for the aerosol fumigators.

Fluosilicic Acid and The Silicofluorides

The position of fluosilicic acid and its salts is unique as far as a fluorine chemical industry is concerned. The fertilizer phosphate industry confronted with a disposal problem of by-product gases that contain fluorine, developed a silicofluoride chemical industry. In other words, fluorine has always been considered a necessary evil by the phosphate interests. The magnitude of this by-product fluorine has been pointed out already, and its potential implications for the future cannot be ignored. Even though the phosphate industry is considered almost the exclusive producer of silicofluorides, the anhydrous hydrofluoric acid manufacturers also produce a small amount of this material as a secondary product. It should also be pointed out that it is possible to develop a silicofluoride industry based on low-grade fluorspar (high in silica) if economic conditions ever warrant it.

In the acidulation process for the manufacture of fertilizer phosphate, the rock phosphate is treated with sulfuric acid and approximately one-half of the fluorine is evolved in the form of a gaseous mixture. This toxic gaseous mixture of hydrofluoric acid, silicon tetrafluoride, and fluosilicic acid is passed through water absorption towers. Fluosilicic acid (H_2SiF_6) and a precipitate of silica are formed. Approximately one-half of the fluorine in the gases is recovered in this process. The fluosilicic acid liquor is concentrated to commercial strengths by recycling or distillation.

Fluosilicic acid is sold generally in strengths of 30 to 35 percent, although other concentrations are available. A large use for this acid is in

the brewing industry as a disinfectant for copper and brass vessels. It is sold also for use as a preservative, in electroplating, as a concrete hardener, and in the manufacture of silicofluoride salts.

Sodium silicofluoride (Na_2SiF_6) is the most common salt, and is readily prepared by the addition of sodium chloride or soda ash to the acid. It precipitates from solution as a white finely-divided product. In many recovery plants this salt is considered as the sole means of disposal. It is used extensively as an insecticide, laundry sour, fluxing and opacifying agent in the ceramic industry, and as a protective agent in the casting of light metals. With a production of over 10,000 tons in 1944, its value for that year can be estimated to be about one million dollars.

Ammonium fluosilicate is prepared by neutralizing fluosilicic acid with strong ammonia. This salt is used extensively in the laundry and light metal casting industry. The magnesium and zinc fluosilicates also are prepared from the acid by neutralization. Both salts are used as concrete or wall hardeners, and the magnesium salt finds application also in magnesium foundries. The zinc and copper salts are useful as impregnating compounds for the prevention of wood decay. Barium silicofluoride is a common insecticide and is also used in ceramics. Lead fluosilicate is used primarily in the electrolytic refining and plating of lead. Occasionally salts such as calcium, iron, aluminum, cobalt, nickel, and potassium are mentioned as having special limited uses. It is interesting to note that zinc, magnesium, copper, and lead fluosilicates are all quite soluble in contrast to the sodium and potassium salts.

Synthetic Cryolite and Aluminum Fluoride

The aluminum industry is one of the heaviest consumers of fluorine compounds. Cryolite comprises the molten bath in the electrolytic cells. Aluminum fluoride and fluorspar are added directly in small amounts from time to time while the cells are operating. It is difficult to arrive at exact consumption figures for each component, although it is stated that 0.1 lb. of cryolite is required for each pound of metallic aluminum produced. On this basis, 60,000 tons of cryolite was required in 1947 to produce 600,000 tons of aluminum.

It has long been known that the aluminum industry is not dependent upon natural cryolite and is consuming large quantities of the synthetic material derived from fluorspar. Unofficial statements indicate that the natural cryolite is favored usually when the cells are put into operation. In general, synthetic cryolite is prepared by reacting a mixture of alumina and hydrofluoric acid, and neutralizing it with soda ash or alkali. A more recent process was mentioned previously. The synthetic processes enable the manufacturers to produce a uniform and high quality cryolite. Aluminum fluoride can be readily prepared by simply reacting alumina with hydrofluoric acid.

Both synthetic cryolite and aluminum fluoride are used in the ceramic industry. The insecticidal industry of-

fers a ready market for cryolite, especially in the form of fruit orchard sprays. One of the prerequisites for insecticidal purposes is that the material be very finely divided in order to be effective.

Minor Fluorine Chemicals in Industry

The fluorine chemicals discussed in this section have been arbitrarily grouped together for the sake of brevity. Some compounds may be produced in tonnage lots at a fairly low unit cost, whereas others may have a limited market and demand a high price. The real purpose of this discussion is to point out the wide range of uses along with the wartime and more recent developments of the fluorine industry.

Inorganic Fluorides

Simple inorganic fluorides may be classified into two groups, depending upon their stability in water. Those stable in water solution can be prepared by reacting their carbonates, oxides, or hydroxides with aqueous hydrofluoric acid. This group comprises practically all of the well known fluorides. Some of them form acid fluorides with an excess of acid. The double fluorides are obtained by reacting two basic components in the proper proportions in hydrofluoric acid. The second group, fluorides which hydrolyze in water, are prepared usually from the chlorides with anhydrous acid; examples of this group are boron trifluoride (BF_3) and antimony pentafluoride (SbF_5). Still another group of fluorides requires gaseous fluorine in their synthesis. Examples are cobalt trifluoride (CoF_3), chlorine trifluoride (ClF_3), sulfur hexafluoride (SF_6), and uranium hexafluoride (UF_6).

The uses of inorganic fluorides extend over a broad range, but relatively few are used in tonnage lots. Most common salts are the sodium, ammonium, potassium, barium, zinc, magnesium, chromium, aluminum and antimony salts. The sodium, potassium, and ammonium salts find use in preservatives and insecticides (a common roach powder uses sodium fluoride). The ceramic industry utilizes salts of lithium, sodium, copper, beryllium, barium, strontium, zinc and aluminum. Beryllium fluoride and its sodium double salt are used in the production of metallic beryllium. Sodium fluoride is used in the steel industry for promoting soundness in the outer layer of a steel ingot and in rim steel production. Zinc fluoride is used in insecticides and for wood preserving. The chromium salt finds application in the textile printing and dyeing industries. Antimony, mercury, zinc, and potassium fluorides are used in the synthesis of organic fluorine compounds. Boron trifluoride is used as a catalyst in the manufacture of some synthetic rubbers and fine organic chemicals. Rare earth fluorides are used in the cores of carbon electrodes for anti-aircraft searchlights. Synthetic fluoride crystals of lithium and calcium are used in optical instruments. Cobalt trifluoride finds extensive use in the synthesis of fluorocarbons. Chlorine trifluoride was contemplated for use in incendiary

bombs, and can be used in certain types of fluorinations. Due to its high dielectric value, sulfur hexafluoride is used as a gaseous insulator in x-ray equipment and the like where extremely high voltages are involved. It possesses the additional features of being non-toxic, extremely stable (more inert than nitrogen), noninflammable, and five times as heavy as carbon dioxide gas.

Uranium hexafluoride, UF_6, merits special attention because of its basic use in atomic energy and the first "atom bomb." Uranium possesses certain isotopes required for nuclear reactions, and in order to separate and concentrate these isotopes by some suitable means, it became necessary to find a thermally stable uranium compound with a high vapor pressure near room temperature. The only compound meeting these specifications is UF_6 with a sublimation point of 56° C. In other words, a fluorine compound was instrumental in opening the door to an atomic energy world. The amount of uranium hexafluoride which has been produced or will be in the future is relegated appropriately to the secret archives of the Atomic Energy Commission.

In commerce, the acid fluorides are usually represented by the sodium, potassium, and ammonium salts. They are used as laundry sours, for etching glass, in welding fluxes, and in fusion mixtures for the extraction of various metals. The potassium salt is used exclusively in the commercial preparation of fluorine. Fluoboric acid, HBF_4, is used in electroplating, aluminum reflectors, and in the manufacture of dyes and organic fluorine chemicals.

Among the double salts, synthetic cryolite, Na_3AlF_6, is the most important. Sodium antimony fluoride is used as a mordant in dyes and in the synthesis of organic-fluorides. The sodium, potassium, and ammonium fluoborates find application as sand agents in the casting of aluminum and magnesium, in electro-chemical processes, and chemical research.

Fluorine Gas

Henri Moissan in 1886 succeeded in preparing fluorine, as a free element, by the electrolysis of potassium acid fluoride. Almost sixty years elapsed before scientists in Germany and the United States solved the problem of handling fluorine safely and producing it in large quantities. It is interesting to note that this was achieved almost simultaneously and independently by two groups of scientists on opposing sides during World War II.

Two types of cells have been developed, one operating at about 100° and the other at 250° C. Both types use potassium acid fluoride as the electrolyte and anhydrous HF is fed into the cells to maintain the proper composition. According to reports from Germany, 2,000 ampere cells operating at 8-15 volts with a current efficiency of 95 percent were capable of producing almost 2,000 pounds of fluorine per month. They reached a total output of 50 tons of fluorine per month. The fluorine gas is piped through steel or copper pipes, and stored in steel cylinders. Small laboratory cells are available as well as small cylinders of fluorine for experi-

mental purposes. Fluorine being the most reactive element known, unusual precautions must be strictly observed in its generation, handling, and application.

The uses of fluorine are very limited at the present time. Presumably, large quantities were and are being used in the preparation of uranium hexafluoride from a uranium oxide for nuclear reactions. Sulfur hexafluoride is prepared by the direct combination of sulfur and fluorine. Higher metallic fluorides (CoF_3, AgF_2, CeF_4, MnF_3, etc.) and halogen fluorides (ClF_3 and BrF_3), useful in certain organic fluorinations, can be prepared only by the use of fluorine gas because of its high oxidation potential.

One of the methods developed during the war for the production of fluorocarbons involves the direct fluorination of organic compounds. These compounds and other methods of synthesis are discussed later.

Organic Miscellanea

The synthetic organic chemical industry, with its diversity of compounds and extensive applications, offers unlimited opportunities for the development of organic fluorine compounds in many fields of interest. In order to show that this industry is begining to recognize these possibilities, a number of compounds which have appeared in the trade are discussed.

Dyes and Dye Intermediates

The I. G. Company of Germany introduced a group of fluorine-containing dyes to the American market in the 1930's. These brilliant dyes of yellow, orange and red colors exhibited unusual color clearness and possessed excellent light and laundry fastness. Fast Orange Salt RD and Fast Orange Golden Salt GR are two examples of this group, and supposedly they are benzotrifluoride derivatives. Benzotrifluoride ($C_6H_5CF_3$) is a very stable organic fluorine compound and the American production of this compound has been announced recently. It is interesting to note that once these dyes appeared on the market, imports increased each year until the Nazi military machine began its European expansion program.

Concurrently with these dyes, the above company also introduced certain stabilized diazo salts containing the fluoborate radical. In other words, they were diazonium salts of fluoboric acid (HBF_4). Fast Red Salt RL, 2-methyl-4-nitrobenzene diazonium fluoborate, is a typical example. Besides fluoboric acid, certain metallic fluorides, fluorosulphonic acid, and borofluorosulfonic acid can be used as diazo stabilizers.

Fluorocarbons

The "atom bomb" was responsible not only for the large-scale production of gaseous fluorine and uranium hexafluoride, but also for the development of a group of completely fluorinated organic compounds. In order to separate the isotopes of uranium by a gaseous diffusion process, it became necessary to develop a liquid which possessed unusual thermal and chemical stability. The completely fluorinated hydrocarbons provided the answer and are known under vari-

ously coined terms such as "perfluoro" hydrocarbons, "fluorocarbons," and "fluocarbons."

The synthesis of these compounds depended upon the development of controlled methods of fluorination of hydrocarbons without the usual explosions or extensive scission of carbon-carbon linkages. This is due to the fact that fluorine is the most reactive element known, and its heat of reaction is so high that very few organic systems can absorb the heat impact directly without disintegrating. Two general methods were developed, (1) fluorination with gaseous fluorine, and (2) fluorination with CoF_3, etc. It is interesting to compare the heats of reaction in the two methods.

(1) $C_7H_{16} + 16F_2 \longrightarrow C_7F_{16} + 16HF + 1660$ kg.-cal.

(2) $C_7H_{16} + 32CoF_3 \longrightarrow C_7F_{16} + 32CoF_2 + 16HF + 1000$ kg.-cal.

The second method has the lower heat of reaction, due to the fact that part of the energy has been dissipated previously in a separate system in converting CoF_2 to CoF_3. Complete details of both methods of fluorination and the various fluorinating agents which can be used have been described in the March 1947 issue of *Industrial and Engineering Chemistry*.

A new and novel process for the preparation of fluorocarbons has recently been announced by Simons and co-workers which appears to accomplish the same objectives as direct fluorination. It is an electrochemical process involving the electrolysis of organic substances in liquid hydrogen fluoride.

One of the uses for the liquid fluorocarbons has been mentioned already in connection with the atom bomb. Due to their unusual stability and non-inflammability, their use as lubricants, coolants, and hydraulic liquids has been suggested.

Plastics

Today there are two fluorine-containing plastics on the market. Teflon derived from tetrafluoroethylene is produced by the duPont Company. The other, Kel-F, derived from trifluorochloroethylene is marketed by the M. W. Kellogg Company.

Both plastics are produced from a Freon type of compound. They are non-inflammable, insoluble in organic solvents, very stable to chemical agents, possess high thermal stability, and are excellent dielectric materials. One of the first uses for Teflon was a gasket material in fluorine cell construction. Due to their high cost they will find use only where very unusual conditions exist.

Insecticides—DFDT

During the recent war, in Germany considerable use was made of a fluorine compound related to DDT. It is called DFDT and chemically it is known as 4,4'-difluorodiphenyl trichloroethane. Instead of using chlorobenzene as in the synthesis of DDT, fluorobenzene is used. Production of DFDT must have reached sizable proportions, as fluorobenzene was produced at the rate of 12 tons per month for the manufacture of this insecticide. It appears that for certain insects it is more effective than DDT. The production cost of this insecticide is considerably higher due to the higher cost

of fluorobenzene over that of chlorobenzene. It remains to be seen if this insecticide will find a place on the American market.

"1080"

During the war years the sodium salt of monofluoroacetic acid ($CH_2FCOONa$) was discovered to be the most toxic rodenticide known. For secrecy reasons it was given the code number "1080." It possesses high toxicity to all rodents tested, excellent acceptance, quick action, absence of objectionable taste and odor, chemical stability and non-volatility, and lack of toxicity to the skin. Its distribution is very carefully controlled, as it is very poisonous also to humans if taken internally, plus the fact that there is no known antidote for it.

The commercial process for its manufacture has been described by Jenkins and Koehler. About 10,000 pounds per year meet the present commercial demand. During the war it was used extensively for rodent control around military installations.

"There is nothing new under the sun" aptly applies to "1080." Nature has endowed a plant in South Africa with the ability to synthesize this toxic principle, and its identification in the plant was not accomplished until 1944 by Marais. This is the first recorded synthesis of an organic fluorine compound in nature. To add a bit of irony to the great war secret, the natives in the natural habitat of the plant have been aware of its poisonous properties to cattle and rodents for many years.

Drugs

Pardinon (3-fluorotyrosine) and Epidermin (4,4'-difluorobiphenyl) appeared on the German drug market before the war. The sodium salt of *para*-fluorobenzoic acid has been mentioned as an internal antiseptic. Diisopropyl fluorophosphate, called DFP, is a very toxic material, but in very low concentrations it can be used in medical work.

Future Prospects in Fluorine Chemistry

After reviewing the position of fluorine and its compounds in industry, it is obvious that fluorine chemicals are finding their industrial niches by the impact of their unique properties. By the same token, industry has found a new tool in fluorine chemistry that has fabricated and will fabricate for tomorrow new products of majestic quality. In view of these facts, it is very much to the point to discuss briefly some fundamental concepts of fluorine chemistry. Fluorine is the most reactive and electronegative element known. It has the distinction of being the first member of the well-known halogen family (F, Cl, Br, and I). Due to its distinguished position in the family, the element and its compounds exhibit not only some of the usual family characteristics, but many unique properties quite foreign to the other members. These concepts lead to a research philosophy that anything can happen in fluorine chemistry. The achievements of the last decade are but a feeble introduction

to the many frontiers still waiting to be challenged and probed. In short, fluorine promises to write one of the most brilliant chapters in academic and industrial chemistry.

A synthetic fluorine chemical industry is based essentially on fluorspar and hydrofluoric acid, and an industrial fluorine economy will continue to revolve around these basic materials for many years to come.

Much has been said about the availability of fluorspar, the primary raw material. It is true that it is a strategic mineral, but by shifting the demand for metallurgical spar under emergency conditions, through a good neighbor policy, to Mexico and other sources, the domestic industry should be able to produce adequate tonnages of acid spar for many years. This is further enhanced by the fact that the Illinois-Kentucky fluorspar district has the facilities, the "know-how," and the capability of producing increased tonnages of high grade acid spar of constant and uniform quality.

Very little needs to be said about hydrofluoric acid, the key chemical, except in retrospect. It is available in all strengths, on a large tonnage basis, and at a fairly reasonable price. It is interesting to note that the demand for the acid is increasing steadily since the war recession. This means that the chemical industry is expanding its fluorine chemical interests in a peacetime economy.

Research and development in fluorine chemicals is no longer relegated to the isolated recesses of a few intrepid academic investigators. Modern technology has solved many of the difficult problems of handling, control, and operation. In fact many process industries are capable of embarking upon a fluorine program because of the calibre of their research staffs, experience in handling other operations just as hazardous, and the availability of modern equipment. Immediate success is not to be expected, but a long-range program based upon an experienced and capable staff, and synchronized with materials already within the organization, is bound to achieve commercial objectives.

The opportunities for research with fluorine chemicals is almost unlimited. Since fluorine in its compounds exhibits very unusual properties, advantage must be taken of the unusual. Fluorine compounds will be expensive and they must find their place on the industrial market where their superiority will not have any close competitors. In general, fluorine exhibits unusual stability in its compounds in contrast to chlorine or other halogen atoms. There are many changes in properties, induced by it in compounds, such as volatility, surface tension, index of refraction, etc. Such fields as solvents, plastics, medicine, pharmaceuticals, dyes, insecticides and many others offer unusual opportunities. Fluorine compounds run the extreme in toxicity; some are as inert as nitrogen, whereas others such as "1080" are very poisonous. Very few studies have been made on toxicity and the effect of fluorine in biological systems. In retrospect, fluorine chemistry is one of the newest fields of chemical endeavor and promises to increase in stature in the future.

Hydrocarbon Sulfonylation

Synthetic Detergents

by Burton L. Hawk

➤ Every so often we read of a process simple in its concept yet complex in its result, utilizing inexpensive raw materials, yet producing valuable products. Such a reaction is the sulfonylation of hydrocarbons. The inexpensive raw materials are salt, sulfur, and paraffin. The simple process consists of bubbling sulfur dioxide and chlorine through paraffin. The complex result is the formation of soluble compounds of the polyhydric alcohol type. The valuable products are wetting agents important in the textile, paper, and leather industries. As excellent detergents they find use in many "synthetic soap" preparations.

The above reaction can be performed in the home laboratory. The formation of a water-soluble product from paraffin makes a fascinating experiment.

As outlined above, our chief objective is to maintain a steady flow of sulfur dioxide and chlorine, passing the mixed gases through melted paraffin. There are a number of methods by which this can be done. We are suggesting one such method here; you may, of course, use your own initiative to improve or modify this method depending upon the facilities of your home lab. As shown in the accompanying diagram (Figure 1), the gases are generated in flasks A and B. The sulfur dioxide is formed by dropping dilute hydrochloric acid on sodium bi-sulfite or sodium sulfite. The chlorine is obtained by adding dilute hydrochloric acid to manganese dioxide or to a *solution* of potassium permanganate. In both cases the acid is added frequently and in small quantities. Gentle heat is supplied under both flasks to insure a steady flow of gas. Occasionally more sodium bisulfite or potassium permanganate may be added as required. It has been found that better results are obtained if an excess of sulfur dioxide is used. In this set-up it is rather difficult to regulate the quantity of gas formed; however, give preference toward the production of sulfur dioxide by using more chemicals in greater concentration, more heat, etc.

The paraffin may be of the grocery store variety—the type which grandmother used to seal her jars of homemade jellies. A small quantity is placed in flask C and melted by applying gentle heat. Thereafter supply just enough heat to keep the paraffin in a molten state. There is some risk of explosion with high temperatures, so you will want to avoid over-heating.

The gases should be thoroughly dried before they enter the paraffin flask. Use calcium chloride tubes filled with anhydrous calcium chloride for this purpose. These tubes are not

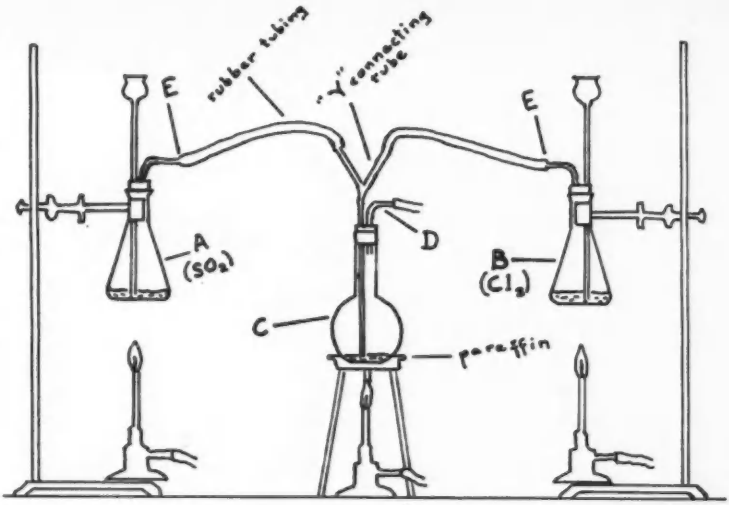


Fig. 1

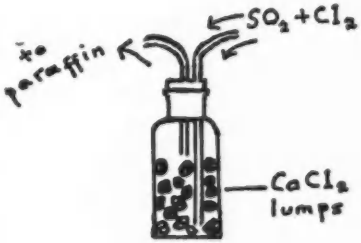


Fig. 2

shown in the diagram; however a suggested place for them is indicated at points E. An alternate method of drying the gases is to allow them to flow through a small jar loosely filled with calcium chloride lumps as shown in Figure 2.

A rubber tubing should be attached to outlet tube D on the paraffin flask to lead the exhaust gases away, preferably to an open window.

The actinic radiation furnished by an ordinary 100-watt tungsten light bulb has a beneficial effect on this reaction; therefore, arrange to suspend such a bulb near the reacting flask.

Now you should be ready to start the reaction. Make sure all connections are tight. First melt the wax, then add HCl to the generating flasks and apply heat. (Alcohol lamps will serve very well in supplying the heat required for this experiment). The gases should bubble through the paraffin slowly and steadily. Be not deceived, this experiment is not so easily performed as described. It will require patience and ingenuity. The reaction must be carried on for a long time, the actual length depending upon the

rate of flow, ratio of two gases, heat applied, etc.

The desired product of this reaction should be light yellow in color, viscous, and liquid at room temperature. If the liquid assumes a dark color, the temperature is too high. This will result in polymerization which is not desired in this case.

Failure to obtain the above described product may be due to a number of causes. Foremost to consider is the length of time required. The reaction should be run for *at least* six hours—probably longer. No doubt it will be necessary to stop the process and continue it at another time. It is advisable to replace the generating flasks, A & B, several times using a fresh supply of chemicals. Remember, a *slow*, steady stream of gas is preferable. Also, shaking the paraffin flask occasionally will help.

The final step is the hydrolysis or saponification of the paraffin product. Pour a portion of the hot oily liquid slowly into a warm dilute solution of sodium hydroxide. Stir thoroughly, and allow to stand for an hour or two. The resulting solution should be reasonably clear. Separate from any undissolved oily layer that may be present, and evaporate to dryness. The resultant yellow or white powder will dissolve in water to a clear solution. Experiment a bit with this solution. You will find that it has excellent detergent properties, foaming action, and wetting power.

Synthetic detergents are still relatively new. Although they are becoming more and more popular, the full extent of their usefulness has not yet been realized.

Quick New Test Aids Diagnosis

➤ A SIMPLE, quick test for determining the amounts of individual plasma proteins in blood shows promise of aiding in the diagnosis of liver diseases, tuberculosis, and other ailments.

A minimum of equipment and two drops of blood are required and it can be performed "in a country doctor's office or on a battlefield," Patterson B. Moseley and Dr. Arthur L. LeRosen of Louisiana State University told the Fourth Annual Southwest Regional meeting of the American Chemical Society.

The chemists explained that the blood drops are mixed with a sodium sulfate solution and poured into a glass tube packed with a special absorbent clay known as diatomaceous earth. The albumin of the blood is washed away by pouring the sodium sulfate solution through the tube and the other plasma proteins can be removed separately by washing with other salt solutions. Ultraviolet will then show the amount of each protein present by the amount of light it absorbs.

Diseases such as cirrhosis and cancer of the liver and tuberculosis are known to disturb the balance of proteins in the blood. If, for example, the test revealed a high content of fibrinogen, protein responsible for clotting, the physician would suspect tuberculosis and other lung disorders.

How Salt Substitute Kills Is Found in Experiments

Lithium Chloride Death Cause

➤ THE WAY in which lithium chloride causes death has been discovered by Dr. John MacLeod, of the Cornell University Medical College, New York.

His experiments on rats show that lithium in low concentrations produces an inhibitory effect on the breakdown of glucose to lactic acid, one of the fundamental processes in the use of food by the body.

Deaths reported in patients with heart and kidney disease who use lithium chloride instead of ordinary sodium chloride salt in their diet are thus shown to have an experimental theoretical basis.

Dr. MacLeod's conclusions will appear in a paper ready for publication in the *American Journal of Physiology* and were made available to Science Service on account of their relationship to the dangerous use of this chemical medically. The work was completed two years ago as a purely academic study and is only ready for publication now.

Dr. MacLeod found the inhibitory effect in human spermatozoa and he found that it destroyed the ability of these cells to move. When lithium chloride was injected under the skin of rats (dosage level of 120 milligrams per kilogram) it caused too much irritability in the rats, weakness of hind legs, and generalized tremors which appeared particularly when the rat was stimulated. In general such an acute dose of lithium chloride produces death in rats within 28 hours.

The chronic effects of injecting small doses of lithium chloride in rats daily over protracted periods, Dr. MacLeod found, is to produce such symptoms when an injection level of five milligrams daily and a total level of 150 milligrams is reached. This indicates that lithium is retained in the body, in part at least, possibly in the muscles.

Dr. MacLeod concludes that there is considerable resemblance in the effects in rats and the symptoms in human beings by analogous intakes of the salt. If the doses producing the effects in normal rats are extrapolated on a weight for weight basis to humans, an intake in the human of from 1.4 to 2.8 grams daily of the salt theoretically would produce symptoms in from two weeks to a month. (One gram is about a thirtieth of an ounce). Dr. MacLeod emphasized that this is theoretical and may have no relationship to the doses taken in the human toxicity cases recently reported.

Muscular weakness, one of the characteristic symptoms, is due, it is suggested, to interference with carbohydrate breakdown in the skeletal muscles. Lithium chloride might impose an extra strain on an already deficient heart, in cases of cardiac deficiency on a salt-free or salt-substitute diet.

Fibers, Foods, and Minerals Treated by New Processes

Patents on Chemical Materials

To obtain copies of patents, order by number, enclosing 25 cents in coin, money order or Patent Office coupon. Address Commissioner of Patents, Washington 25, D.C.

➤ A CHEMICAL process for retting flax, hemp and similar textile fibers obtained from plant stalks is covered by patent 2,457,856, issued to Jacob J. Zeehuisen of Scheveningen, The Netherlands. In the traditional process, which is older than history, the stalks are placed in tanks of water, and enzymes secreted by bacteria break down the short-celled tissues that bind the fibers together. In the present invention, these largely unidentified and ill-controlled enzymes are replaced by a solution containing hydrogen peroxide, ammonium phosphate and urea, and the digestive process of retting is carried out much more rapidly at a temperature near the boiling point of water.

Blood Fiber Sutures

Surgical sutures made from the fraction of human blood left after the extraction of plasma are the subject of patent 2,457,804, issued to John O. Bower of Wyncote, Pa. Chemical treatment of this fraction reduces it to fibrous form, and the fibers are processed into sutures.

Oil Under Pressure

Getting oil out of oil wells through the use of gases under pressure instead of by the conventional pumping method is the basis of patent 2,458,053, obtained by a Scottish engineer, Norman Fraser Brown, of Stow. The gas is forced intermittently into a displacement chamber immersed below liquid level in the well.

Hydrogen Fluoride

➤ HYDROGEN FLUORIDE, a powerful acid much used in chemical industry, is purified more effectively and cheaply by a process on which three researchers for the Allied Chemical and Dye Corporation of New York, A. C. Hopkins, Jr., R. M. Stephenson and W. E. Watson, have taken out patent 2,456,509. As produced by the treatment of fluorspar with sulfuric acid, the crude hydrogen fluoride contains silicon fluoride and other impurities. The three chemists have found that fluosulfonic acid, with the formula H_2SO_3F, will absorb hydrogen fluoride but not the impurities. Subsequent mild heating releases the hydrogen fluoride in pure form.

Lead Plating

A method for plating iron or steel with lead, for protection against corrosion, is covered by patent 2,456,235, issued to William Yonkman of Chicago, assignor to the Western Electric Company, Inc. The cleaned articles to be plated are first dipped in a fluxing bath of zinc ammonium chloride, then immersed in a bath of molten lead containing some antimony.

To Make "Puffed" Rock

Various kinds of fluffed-up rock, produced more or less on the same

principle as puffed breakfast grains, have recently become popular for purposes ranging all the way from potting houseplants to lightweight aggregate for concrete. A new one is offered by John L. Fournier of Los Gatos, Calif., for patent 2,455,666.

Raw material is the dark, obsidian-like type of lava known as perlite. This mineral, ground to suitable size, is fed into one end of a long crucible consisting of a series of frustro-conic segments. A heating flame also blows into the feed end, and air blasts from a series of annular vents help to maintain temperature and also carry the heated material along. At the discharge end the transformed perlite comes out much reduced in density and of a whiteness that makes the name more appropriate.

Rotating Steel Maker

A rotating converter for steel-making, that looks like a Dantesque version of a concrete mixer, is covered by patent 2,455,531, assigned to the Petersen Oven Company of Chicago by the inventor, Jack L. Stroman of Elmwood Park, Ill. By arranging to have both air blast and discharge on the same side, Mr. Stroman has considerably increased the capacity of his machine over conventional models of the same type.

Liver and Egg Products

Two new special food products, of value in the diet of infants and invalids, the one from liver, the other from eggs, are among recent chemical patents.

The first, covered by patent 2,454,837, was developed by Prof. James A. Reyniers of the University of Notre Dame. In preparing it, finely minced liver is subjected for 20 hours or more to a pressure of about 600 pounds per square inch, at a temperature of 50 degrees Centigrade, in the presence of carbon dioxide. This converts the liver protein into something much more readily amenable to delicate human digestions. Rights in the patent are assigned to Amino Acids, Inc., of Wilmington, Del.

The second product is made by first centifuging egg yolk, to separate out gross solids, then subjecting the fluid to solution in ether. This splits it into three layers, the middle one of which contains the desired substance, known as lipovitellenin. This product has been prepared by two U.S. Department of Agriculture workers, Dr. Harry L. Fevold and Miss Adele Lausten Dimick; they have assigned rights in their patent, No. 2,454,915, royalty-free to the government.

Soil Treatments

Potash is extracted from the mineral known as wyomingite by treatment with sodium carbonate solution under steam pressure, in the process on which patent 2,455,190 was granted to Robert D. Pike of Pittsburgh.

The acidity and oxidation-reduction potential of soil, factors of importance in determining liability to corrosion of pipelines and other soil-covered structures, are determined by electrical measurement in the method on which patent 2,454,952 was issued to R. L. Starkey of New Brunswick, N.J., and K. M. Wight of Philadelphia. The electrodes are contained in a pointed casing that is plunged into the soil, which is then permitted to enter and contact them.

Improved Leather Sewing

➤ BETTER SHOES are promised with a method of using glue instead of wax on the thread used in sewing machines for stitching heavy leather. The glue has a tougher, more durable sealing action to lock the threads of a seam in position after insertion, the inventor of the glue-applying equipment states. The glue coating has long life and glue-treated thread retains flexibility.

The idea of using glues of several different types instead of wax on the sewing thread, to hold loose fibers down and lubricate it so that it may be drawn through the leather, is not new. Application has been delayed because of difficulties encountered in coating the thread with a thin uniform film. The equipment just patented accomplishes this.

Recipient of the patent, 2,454,277, is James P. Fredericksen of Braintree, Mass. The patent, entitled the "art of sewing," has been assigned to the United Shoe Machinery Corp., Flemington, N.J.

Cotton Explodes With Fluorine

➤ORDINARY COTTON and low-temperature liquefied fluorine will explode violently on mere contact, it has been discovered during research for the Atomic Energy Commission.

Because the exceedingly poisonous and corrosive fluorine is increasing in importance as a specialized industrial chemical, especially in atomic energy work, protective measures were studied at Oak Ridge, Tenn., by R. H. Lafferty, Jr., J. C. Barton, and J. A. Westbrook of Carbide and Carbon Chemicals Corp. Their warnings appeared in the American Chemical Society journal, *Chemical and Engineering News.*

These chemists made their test working in gas masks and heavy gloves and protected by a safety barricade and a ventilating hood to carry away the dangerous fumes. Their object was to find the protection given by ordinary industrial workmen's gloves. A fingertip cut from a neoprene glove was first lowered into a tiny pool of the liquefied fluorine held at 209 degrees below zero Centigrade by liquid nitrogen cooling. The neoprene caused a puff of a small explosion and burst into flame. Next a leather glove was tried, but it merely charred and smouldered and did not break into flame.

The instant the tiny tip cut from a cotton glove touched the liquid fluorine there was a violent explosion and a brilliant white flame. The force of the explosion cracked all the safety glass in the room, bent and distended the stainless steel container which held the fluorine, and 100 feet down the hall gave a noise like the crack of a high-powered rifle.

The dangers from liquefied fluorine came as no surprise, since as early as 1903 Moissan and Dewar found that fluorine, even in the liquid form, would react explosively with turpentine, anthracene, or liquid hydrogen.

Problems in Safe Handling of Atomic Power Plant By-Products

Radioactive Waste Disposal

Atomic disintegrations, once set in motion, cannot be stopped or modified by any chemical treatment. When waste materials from nuclear reactions are giving off radiation in dangerous amounts, special precautions are necessary in disposing of such wastes.

The Atomic Energy Commission held a symposium in Washington recently, to acquaint sanitary engineers, and others professionally interested, with methods useful in coping with radioactive by-products.

The following papers from that symposium, continuing the series published in the February issue of CHEMISTRY, *tell of handling the waste products from nuclear reactors.*

Cooling Fission Products

by ARTHUR V. PETERSON
Division of Production, Atomic Energy Commission

I HAVE BEEN asked to indicate briefly the nature of the disposal problems involved between the acquisition of raw materials and the production of U-235 and Plutonium.

The major portion of the production operations is concerned with the processing of normal uranium and involves disposal problems identical with those encountered in industrial operations except for the very small activity contained in the uranium. The nature of the hazards and the control measures involved in this portion of the operations are such that there is little question that plants employed in this work can be located in or near large cities with adequate safety. The operations here involved include the beneficiation of raw materials, the manufacture of feed materials for both Oak Ridge and Hanford, and the production of U-235 at Oak Ridge.

The operations at Hanford involve the handling of large amounts of highly active materials and in this respect differ uniquely from normal industrial operations. The steps involved and the nature of the disposal problems are briefly set forth as follows: Canned uranium slugs are charged to the piles. The fission reaction which takes place when the piles are operated results in the formation of Plutonium and highly active fission products within the slugs themselves. Heavy shielding around the piles holds back the fission product emanation. The heat generated by the reaction is of considerable magnitude and must be removed. The piles are cooled by water from the Columbia River which has been pre-treated to remove impurities. In passing through the piles, the water is subject to irradiation by neutrons and the remaining impurities become slightly active. The water containing these active impurities is detained in

large basins and allowed to "cool" before being discharged to the river. All of the operations are carefully monitored, and the activity level of water discharged to the river is too low to cause injurious effects either to the fish or subsequent users of the water below the plant. After irradiation for an appropriate time, the uranium slugs, now containing fission products and plutonium, are discharged and permitted to "cool" before separation of the plutonium and fission products is undertaken. The subsequent chemical operations are conducted by remote control in heavily shielded buildings. The off-gases resulting from the dissolving operations are scrubbed and filtered and vented through stacks. The resulting solutions are chemically treated for the removal of plutonium and fission products, and the waste materials containing the active fission products are sent to underground storage tanks for retention.

From the inception of the atomic energy project waste disposal has been recognized as a major problem. A broad program directed to determining safe tolerances, developing monitoring techniques, and reducing to a minimum all possible hazards, has been continuously under way. The entire production process, from the initial ore operations through the production of Plutonium has been subject to continuous inspection and control.

MR. WILLIAM RUDOLFS *(New Jersey Agricultural Experiment Station, New Brunswick, New Jersey):* As I understand, the wastes produced from the stacks and from cooling waters are now decontaminated and diffused. You said there are some potential dangers. These potential dangers primarily are that explosions might occur or some accidents might occur?

MR. PETERSON: That is the sense in which I did use the term. The piles contain a great amount of activity as a result of fission products involved. We do not expect the pile to explode from its own causes. Adequate controls have been set up to prevent that. An earthquake may happen or the piles may be bombed or some unforeseen accident arise, which may give rise to a contamination of the area. That is one of the reasons why the particular piles operating at the levels they do with the amounts of activity contained in them have been placed at such remote locations.

MR. ROBERT U. CLARK *(Chief Public Health Engineer, Tennessee Valley Authority, Chattanooga, Tennessee):* You mentioned that there is chemical reaction from the slugs taken out of the pile. Does that give rise to a hazard from the standpoint of stream sanitation besides those that are radioactive, but which may be toxic quite independently of their radioactivity?

MR. PETERSON: All of the wastes at Hanford are discharged from tanks. The acids are neutralized. The liquid wastes are not returned to the river.

MR. BENJAMIN C. NESIN *(Acting Director of Laboratories, Mt. Prospect Laboratory, Brooklyn, New York):* What arrangements do you people propose to make with communities that may be affected by the operation of your plants? I have in mind, for instance, the Brookhaven plant which is almost adjacent to our Long Island water supply system.

CHAIRMAN WARNER: The pile is to be controlled by the meteorological conditions. It won't operate when there is inadequate wind for dilution. While waste liquids might get into your water supply system, the tolerance levels have been set extremely low—practically at the resolution of the instruments.

DR. AEBERSOLD: At Brookhaven there will be no chemical processing of slugs. The slugs discharged from there will be stored underground, not chemically processed, so there won't be a chemical operation. There will be no discharge of any volume for holding tanks. The pile is not water-cooled; it is air-cooled. Therefore, liquid wastes will not pose a serious problem.

MR. NESIN: On that last comment, I understand a whole series of wells are going into that territory there for the purpose of cutting across the ground water flow. Apparently there must be some ground water.

CHAIRMAN WARNER: The U.S. Geological Survey is conducting a study for us there to determine what the problem is.

MR. M. H. GERSTEIN *(Chief Filtration Chemist, Water Purification Division, Chicago, Ill.)*: What are the chances for accidental spills of liquid waste in some of these plants?

MR. PETERSON: I think the chances of accidental spills—you are referring now to chemical operations—may be as good as that in an ordinary plant; however, the operations are carried out in highly shielded cells. If a spill does take place, an attempt is made to flush the cell out and clean it by remote control. The equipment can also be changed by remote control.

If the cell is contaminated to the extent that it cannot be cleaned out, it would be abandoned. We have not had to abandon one yet. If the equipment becomes contaminated to the extent that it will cause trouble in the operations, it will be removed and replaced.

MR. GERSTEIN: Could the spill get to a water stream?

MR. PETERSON: No. The cells themselves are completely contained. The drains would be to the storage tanks.

DR. AEBERSOLD: He means a ruptured slug.

MR. PETERSON: If a slug in a pile is ruptured, that might mean that the material could get out into the cooling water, the retention basin and, if not diverted, into the river. The controls on piles have been set up so that the rupture of a slug can be detected while the pile is in operation. In such an event the pile is shut down, the slug removed and taken out of the system. In the event of a badly burst slug, the water would be held in the retention basin.

DR. ROLF ELIASSEN *(Professor of Sanitary Engineering, New York, N. Y.)*: How about the danger of a spill in transportation from one of your sites to another site?

MR. PETERSON: At Hanford the only hazardous materials transferred in any large quantities are the slugs containing fission products. For transportation between cities, arrangements have been worked out with the railroads and airlines for small amounts of material to be so transported. Where materials to be transported are such that the amounts may cause

activity too great for commercial transportation, special convoys carry the materials with qualified people on hand to take care of an accident that may occur.

MR. W. D. HATFIELD *(Superintendent of Decatur Sanitary District, Decatur, Ill.)*: As I get it, one of the serious problems is these leftover fissionable products that you put underground. You haven't said very much about the eventual disposition of that material or how much of that is produced. Do you have any information on that?

MR. PETERSON: The problem is going to become greater with time as more materials are produced. At the present time we are faced with building storage tanks so that we have enough capacity on hand to hold the material. It is a very costly program. If we could concentrate these wastes to small volume, so as to make our available storage space hold more of the material, the problem would be reduced. A considerable amount of study is being given the problem, so that I don't know how it will be done in the future.

MR. F. H. WARING *(Chief Engineer, State Department of Health, Columbus, Ohio)*: From your remarks, I understand there will be expansion of activities with the establishment of more plants in several states. Will the Commission maintain contact with the state authorities that have authority over water and air pollution to sit down and discuss the possibilities that may come up in the establishment and operation of those plants?

CHAIRMAN WARNER: That is part of the purpose of this meeting, to lay a basis for the situation to be met in that way. It hasn't been done to date, but I hope we can find a way to do that in the future.

MR. PETERSON: I would like to emphasize again that most of our operations do not involve highly active materials. With the exception of the Hanford operations, our plants could be operated close to cities. Plants at Oak Ridge, for example, could be built in the middle of Washington as far as the sanitation and safety disposal activities are concerned. As experience is gained, I think that plants will come closer to cities.

In regard to your question about contacting state authorities and other agencies, the Commission has undertaken, from time to time, to get the advice of many agencies. I have listed a few of the advisory committees that the Commission has in connection with these operations. We have an Industrial Advisory Group which advises principally on industrial and administrative problems. We have a Safety and Industrial Health Advisory Committee. We have a Reactor Safeguard Committee, which looks into these questions of what happens when a bomb is exploded on a plant or on one of these waste tanks. They try to forecast the kind of thing that may take place, for the purpose of trying to make plans for action to be taken or for use in future designs. We have an Advisory Committee on Biology and Medicine. The U. S. Geological Survey, the Bureau of Mines, the U. S. Weather Bureau and many other agencies are contacted in the problems that do arise.

DR. GEORGE J. SCHROEPFER *(Professor of Sanitary Engineering, Uni-*

versity of Minnesota, Minneapolis, Minn.): How can you say you can locate these plants in a city like Washington when you still do not have the solution to the disposal problem?

MR. PETERSON: I was speaking of plants on processing of raw material, on the production of feed material, plants such as we have at Oak Ridge producing uranium 235.

DR. SCHROEPFER: Aren't there chemical processes involved?

MR. PETERSON: Yes, the normal industrial processes. But, as far as the special radiation problems are concerned, they have a much lower degree of hazard because they involve normal wastes.

The raw materials process, the feed material production, involve both the wet and dry processes. Of course, there are some restrictions as far as that is concerned. The point I mean is that the hazards are in the order of magnitude of industrial hazards that one would meet in the course of industry operations. There are no special problems such as we have at Hanford, highly active materials.

MR. FLOYD W. MOHLMAN *(Chief Chemist, Sanitary District of Chicago, Chicago, Ill.):* I assume that the waste in the laboratory in Argonne in Chicago is kept out of the sewers. Of course, there won't be so much danger there from production operations, say, as at Hanford or Oak Ridge.

CHAIRMAN WARNER: I think one can say that the hazard at Chicago has been pretty well studied over and that the limitations of the size of reactor we have and what they do with their waste has been very carefully gone into.

We Must Accept What is There

by ROGER S. WARNER
Director, Division of Engineering, Atomic Energy Commission

➤ NOW THAT we have discussed what radioactivity is, how it appears, what its effect is, and how it has to be handled, we can discuss the processes which are sources of radioactive waste materials. At this point at the atomic energy plant or factory we must accept whatever degree of radiation is present and the permissible limits which have been determined by the biophysicists, and the problem then becomes how to deal with certain given situations.

Radioactive wastes, like chemically toxic wastes, originate in the vast production operations, in the pilot plants and in the laboratories. An engineer must worry not only about safe routine operations, but also the difficulties of maintenance, handling of spills, and the series of circumstances which when coupled together create a major unforeseen contingency.

Most of the operations of ore dressing and feed preparations are not associated with any great quantities of radiation. The largest and the most difficult problems are those directly associated with or resulting from nuclear reactor operations, where the degree of radioactivity is enormous.

The process of fission creates considerable quantities of heat which must be dissipated.

In the case of Hanford, reactors

are cooled by water; those at Oak Ridge and Brookhaven are cooled by air in prodigious quantities. Both methods of cooling involve open cycles without the re-use of coolant. Other coolants will undoubtedly be developed in the future which will involve higher temperatures and closed cycles.

At Hanford, the water is drawn from the Columbia River, treated in the normal manner, pumped through the pile at high velocities, held in a retention basin to permit the decay of such radiation picked up by the soluble salts and then discharged into the river. The exit temperatures may be several degrees above river water but the temperature of the river is not noticeably changed. Actually under normal conditions the chemicals in the water offer more of a hazard than the radiation. The aluminum cartridge which holds uranium fuel slug may rupture on occasion and water may become contaminated above acceptable levels; but in event this happens the water is diverted prior to discharge into the river.

At Oak Ridge and shortly at Brookhaven, air for cooling reactors is filtered for particles before and after use and then discharged into the air through stacks. Argon and other rare gases contained in normal air become radioactive, but the half life radioargon is slightly less than two hours and the volumes are low. Meteorological control of the operation is maintained so that dilution by wind is assured. If the wind is wrong the operations rate is reduced.

Slugs containing uranium, plutonium and fission products ejected from the pile are allowed to cool to permit the decay of a large amount of the short life activity such as iodine.

These slugs are then removed for chemical processing to recover the valuable fissionable material, plutonium. They pass through rather conventional steps of dissolving, precipitating, washing and re-precipitating—operations which are conducted by remote control behind many feet of concrete and using special ventilation. Ventilating air contaminated with particles from this process passes through scrub traps, sand filters and out a stack, again under controlled meteorological conditions.

The liquids increase in volume and hence the radioactivity is reduced from step to step. Ultimately the most radioactive wastes are neutralized and stored in tanks underground. Concentration of these large volumes has not been perfected as yet. Wash wastes are also tanked but after a sufficient period of decay are discharged. This practice was adopted during the war, but it is gradually being superseded as fast as better methods are developed. Before long we can say with assurance that the liquids are completely immobilized and under positive control.

Considerable quantities of contaminated clothing are laundered and tested for re-use. Contaminated trash, biological specimens, etc. are disposed of by burial and more recently in closed cycle incinerators in some areas. Contaminated equipment such as motors, valves, piping is set aside in a burial area. Lead and more recently aluminum shielding blocks used in pilot plant work have been decontaminated for re-issue. Considerable quantities of contaminated

metals of one type or another have been segregated and some effort has been spent to see whether they could be decontaminated satisfactorily enough to put back into commerce. To date such accumulations have remained on Commission sites even though the level of activity is quite low. Contaminated buildings present a problem. After some attempt at decontamination the buildings are usually painted, taken apart board by board and stored in a burial area. Large incinerators with a closed combustion cycle are in design but their feasibility has not yet been established.

In hot laboratories, handling of liquid wastes and ventilation is done in various ways with some degrees of success. No single method stands out for general use. Users of isotopes in tracer work do not as yet run into particularly severe waste problems, because of the low degree of activity.

In brief gaseous, liquid and solid wastes appear at each of the various hot steps. The expedients for disposal used to date have at least stood the test of time. The ultimate goal is improvements in the basic design at the source of the waste rather than attempting to deal with the wastes after they have been produced by such means as filters, and retention basins. These steps will still be necessary, but they will be superseded as the first line of defense. The storage of hot liquid wastes is expensive. It can be endured for a time at one or two locations, but if the industry is to expand as we contemplate, we will ultimately need better means of isolation, concentration, immobilization and control.

There is Time for Study

by DR. PAUL AEBERSOLD
Chief, Isotopes Division, AEC, Oak Ridge

➤ I WOULD LIKE to make these conclusions:

1. The amount of radioisotopes distributed outside the AEC is very small compared with the amounts produced or needed to be disposed of within the Commission. In order of magnitude there is a difference of many millions.

2. Most of the distributed radioisotopes have fairly short half-lives or are elements which are not specifically concentrated in a human body at dilutions encountered after the experiment.

3. Considerable dilution occurs in all tracer experiments and also in most medical experiments, because of the incorporation of material into such a large organism as the human being. There is also subsequent disposal into sewage, resulting in dilution with large amounts of organic matter.

4. There are as yet no large-scale uses in commercial processes, or in any process in which material is incorporated into a product distributed to the public. Also, there are no such amounts used in any industrial process that a large effluence into a sewage system would result. Most of the uses in commercial plants are for tracer research work.

5. The rate of growth of this program is not so rapid that it is likely we will be swamped by a problem of radioactive waste disposal within,

say, a year or two. There is time for necessary studies to be done before distribution of radioisotopes outside the Commission will be a serious health problem.

MR. DAVID B. LEE *(State Sanitary Engineer, State Board of Health, Jacksonville, Florida):* Most of the representatives of the states have in their minds the question: What is going on in my state? What would be the best way for my health officer and sanitary engineer to know about it? They would be the first ones to be asked about it in their state.

CHAIRMAN WARNER: Let me ask, as a small example, Dr. Aebersold, in the distribution of radioisotopes, is it handled much the same way that the Public Health Service would control the distribution of bacterial matter?

DR. AEBERSOLD: We recently have undertaken to send out monthly lists to each public health officer and state health officer, lists of the institutions receiving isotopes during the month.

We plan to visit, if possible, or have the state health officers visit us, to discuss with them the way these things are being used and the measures being taken to prevent their unsafe disposal.

I do not know of any actual cases at the present time in which the state health officers have been taken around to the places where isotopes have been used to show them how they have been used.

We have at Oak Ridge a training course in the use of radioactive isotopes, which lasts for one month. There has been a lot of discussion on how to train people in the health hazards involved in radioactivity, and some people have suggested that we ought to take a year in training a man. It doesn't seem likely that there are many state health officers, or even people on their staffs, who can take a year off to come to Oak Ridge for training. Some public health officers and, probably, some state health officers are in training at various laboratories.

CHAIRMAN WARNER: In your experience to date, for instance in the hospitals in New York City, does everybody use the same high standards?

DR. AEBERSOLD: Most of the hospitals in New York City have a health physicist or a staff member who has had considerable training in the use of radioactive materials.

MR. J. W. KRASAUSKAS *(Bacteriologist, United States Corps of Engineers, Washington, D.C.):* I noted that citric acid, peroxide, and permanganese were used as decontaminating agents for radioactive materials. Why couldn't they be used to dispose of some of these materials?

DR. MORGAN: Those materials are used for decontamination of clothing and hands, and so on. Once the stuff is out of the clothing and off the hands, then there is still the liquid to dispose of .

MR. KRASAUSKAS: I was thinking of radioactive material in the water supplies, and so forth.

DR. MORGAN: We have a group which is working on that problem, making a study of various methods of decontamination. Recent experiments in our laboratory indicate that you can get rid of most of the water by conventional methods, using heat, then store your residue.

MR. R. L. DERBY *(Principal Sanitary Engineer, Department of Water and Power, Los Angeles, California):* There may be some contamination of the marine life. That might depend on the particular isotope which is to be disposed of, or is the danger inherent in all isotopes?

DR. MORGAN: The radioactive material in water behaves exactly the same as stable materials in water. There are certain elements such as radioactive tellurium which are dissolved in the water and stay there; they are not taken out by mud. Most of the materials, however, are taken out rather quickly by mud and plant life in a stream.

MR. DERBY: In the case of ground water supplies, suppose you had some Carbon-14 in the form of an insoluble carbonate or barium carbonate. If the water came in contact with that, would the dissolved material in the water pick that up and carry it on, or would that have very little effect?

DR. MORGAN: If it is insoluble, it probably would not travel very far. As the water passes through the soil, the soil seems to hold radioactivity very well. It probably would not go more than a few hundred yards in a year.

DR. AEBERSOLD: Two things should be made clear. One is that you cannot get rid of radioactivity by any chemical means or even any physical means. When a thing is made radioactive, a certain number of radioactive atoms are made; there is no way in which you can cancel this radioactivity. Either you wait for it to die away, or, if it does not die away, you have to exclude it some place, or else dilute it.

The second point is that the only way of making radioactive material is by bombardment with neutrons or heavily charged particles. Consequently, just coming near radioactive material will not produce radioactivity.

MR. MARTIN HILBERT *(Sanitary Engineer, Wayne County Health Department, Elloise, Mich.):* If a ton of carcasses from some biologic laboratory using Carbon-14 in their experiments is sent to us to burn in an incinerator, are we to understand that there would be no problem because it is being burned in plenty of dilution? Also will the ashes be free of radioactive materials?

CHAIRMAN WARNER: One of the things we are working on is a closed-cycle incinerator that will absorb the radioactivity rather than put it in the air.

DR. AEBERSOLD: The people who do the incineration usually take a Geiger counter, level back the ashes, mix them up with dirt and concrete and bury them at a depth so that they are well diluted.

MR. A. P. BLACK *(Professor of Chemistry, University of Florida, Gainesville, Fla.):* I understand that people in the universities are being supplied with Geiger counters necessary for determining the radioactive count on the bodies of plants and animals. Why can't the same material be made available to the people here?

DR. AEBERSOLD: Geiger counters and ionization chambers and all types of equipment for measuring radioactivity are commercially available from at least forty different instrument-manufacturing companies at the present time.

At Oak Ridge it takes about a

month to learn how to use a Geiger counter and to know what it says after you read it. There are certain symptoms by which you can tell when they wear out or when they are giving a wrong reading. The operator must know these things.

MR. S. T. BARKER *(Chief, Sewage & Wastes Disposal Section, Division of Local Health Services, State Department of Health, Albany, N.Y.)*: I gathered from a little study at Brookhaven that when you plan to discharge wastes into a river, you will find an activity lower, considerably lower, than a Geiger counter will read. Was I misled on that? They implied that in order to prove to themselves that the wastes were not too strong, they were going to have to concentrate them by evaporation, and it was not practical at the levels at which they proposed to operate to use the Geiger counter. I would be very much interested to know whether you can measure a low-level activity with the Geiger counter.

DR. AEBERSOLD: In general, they would have to take a sample of the water and evaporate it down and make a sensitive measurement in order to detect it.

MR. BARKER: So, the health department is not going to be able to survey a stream with a Geiger counter?

DR. AEBERSOLD: Not ordinarily unless evaporation procedures are used.

MR. ROY J. MORTON *(Health Physics Division, Oak Ridge National Laboratory)*: At White Oak, where we are working with higher levels than that, we do not depend on the counter at all. The counter will indicate it, but we still want to evaporate it down and get quantitative measurements.

PROFESSOR ROLF ELIASSEN *(Professor of Sanitary Engineering, College of Engineering, New York University, New York, N.Y.)*: I believe radiocarbon is very little used for obvious reasons; but iodine and phosphorus have half-lives of less than two weeks. We are using Phosphorus-32 in New York and if all the Phosphorus-32 and all the radioiodine were dumped into the sewer, with full strength of activity, the dilution of a billion gallons a day of sewage would give a concentration of 3×10^{-8} microcurie per cc., and as you mentioned here, that is of the order of magnitude of the water supply you have at Oak Ridge.

You must take into account that it does lose its activity, or lose half of its activity, every two weeks or so, and the danger in view of the dilution in the sewage is not very great at the present stage of activity in the various hospitals around the city. The danger that we are worried about is concentration in plumbing fixtures. Suppose a plumber goes to a hospital and it is accumulated in the slimes of these fixtures or other places where it might possibly concentrate, such as in the activated sludge and various places like that.

DR. AEBERSOLD: Our health rules call for the user's surveying any plumbing fixture before any plumber is called in to work with them. If there is any activity in the slime, or anything, then this person is supposed to remove it or else have the plumber wear some rubber gloves or something.

One of the real difficulties is the

problem of public education with respect to radioactivity. I can see bringing a plumber into an institution and saying, "You had better put on some rubber gloves here." He is going to be afraid to touch the pipe.

The point is that tolerance levels are set for people who work with radioactivity or who may be exposed to it continuously. In the case of the plumber who comes in and works on it once every six months or once a year, we set the same tolerance, but the man is protected by a factor of several hundred or thousand by the fact that he does not do this all the time.

CHAIRMAN WARNER: However, you may run into a condition of spills, where even your margin of safety of a thousand, or whatever, is completely inadequate unless the facilities are designed to take the load.

MR. C. J. VELZ *(Professor of Sanitary Engineering, Manhattan College, New York, N.Y.)*: At the rate you are growing now on the distribution of isotopes, 1947-48, how many years have we got to learn this business before we have to worry about it?

DR. AEBERSOLD: Radioactive iodine and radioactive phosphorus are the only ones that are used in large quantities for treatment. Suppose somebody should come along and find a treatment for a widespread disease that was very successful with Carbon-14, which I doubt. Before it ever went into commercial production or was used by the general field of medicine, our advisory committees on this subject, the Isotope Advisory Committee, and the one on Industrial Processing and Waste Disposal, would have to give it very serious consideration. It may be in time, if there is any large scale use of fission products, that those wastes may have to be returned to Commission laboratories. A similar situation might arise with some isotopes. I do not think this would be true of phosphorus and iodine, because they would be decayed before they would get back. In the case of Carbon-14, it would depend on how large the program might be. None of the other isotopes present serious problems except for fission products.

MR. VELZ: I think one of our big troubles is hysteria about the situation, even among our own profession. It is exemplified even by our misunderstanding of the picture among the people who are here today. Certainly, I know among my acquaintances, those who are very worried about plumbing traps and the distribution of these isotopes in various laboratories. I think it would be very helpful to clear the air.

CHAIRMAN WARNER: Of course, one of the points of this session was the hope that you state people would be able to satisfy yourselves, and you would stop some of the emotion that does spread around.

DR. AEBERSOLD: The thing that amazes me is the public hysteria concerned with the distribution of a few curies of activity, when there are possibilities of atomic bombs, with millions and millions of curies. It is a different order of magnitude, yet there seems to be much more importance attached to the small, very beneficial program.

CHAIRMAN WARNER: I am afraid that this meeting cannot go into military aspects. That is in a category we are not in a position to go into.

Burning Coal Underground Yields Good Fuel Gas

New Ways To Use Coal

by A. C. MONAHAN

Why dig coal when it can be made to yield fuel gas merely by burning it underground as it occurs in nature? The answer is simple. The burning process is uneconomical where ordinary operations can be carried out but it seems worthwhile with coal layers too thin for mining.

The process is new. In America it is now undergoing the second experimental trial. In the first, it was proved that gas suitable for firing boilers can be obtained. The gas is also suitable for a source material from which to make synthetic liquid fuels. In this second trial the objective is to find ways to get more gas, better gas and cheaper gas than produced in the first tryout.

This experiment in burning underground coal as it occurs in its natural layers is a joint undertaking of the U. S. Bureau of Mines and the Alabama Power Company. It is being carried out on coal property at Gorgas, Ala., owned by the latter. The first trial was made during 1947. The results are so encouraging that a second testing is now underway.

It is not the thought of the government officials or of the coal operators that underground burning will replace the present types of mining. It is a process for application with coal seams too thin for economical mining and with coal veins too difficult or uneconomical to mine for other reasons.

Basically, the scheme used to obtain combustible gases from coal burning deep in the earth consists of drilling down from the surface through the layer of coal. Fire is started by dropping an incendiary bomb down one or more drill holes. Air, under considerable pressure, is forced down the same hole or holes to feed the fire. The same pressure forces the gases of combustion into other drill holes, and up to the surface.

There the gases are captured and stored, and then may be shipped by pipeline to fire furnaces or used near the location of production to develop electricity. One highly desirable utilization is for the production of synthetic fuels. The process involved is almost identical with that now followed in making heating fuels and gasoline from natural gas.

The 1947 trial was made in a three-foot layer of coal about 30 feet under the surface of the ground. The second trial is to be made in another thin layer, but one that is about 100 feet underground. The earlier experiment showed that the underground combustion can be maintained and controlled, that coal in place can be gasified completely, and that the roof rock settles behind the burning face without cutting off the air or gas.

The gas obtained is a cheap source of carbon monoxide and hydrogen. However, it had a lower heating value than desired. This was thought to be

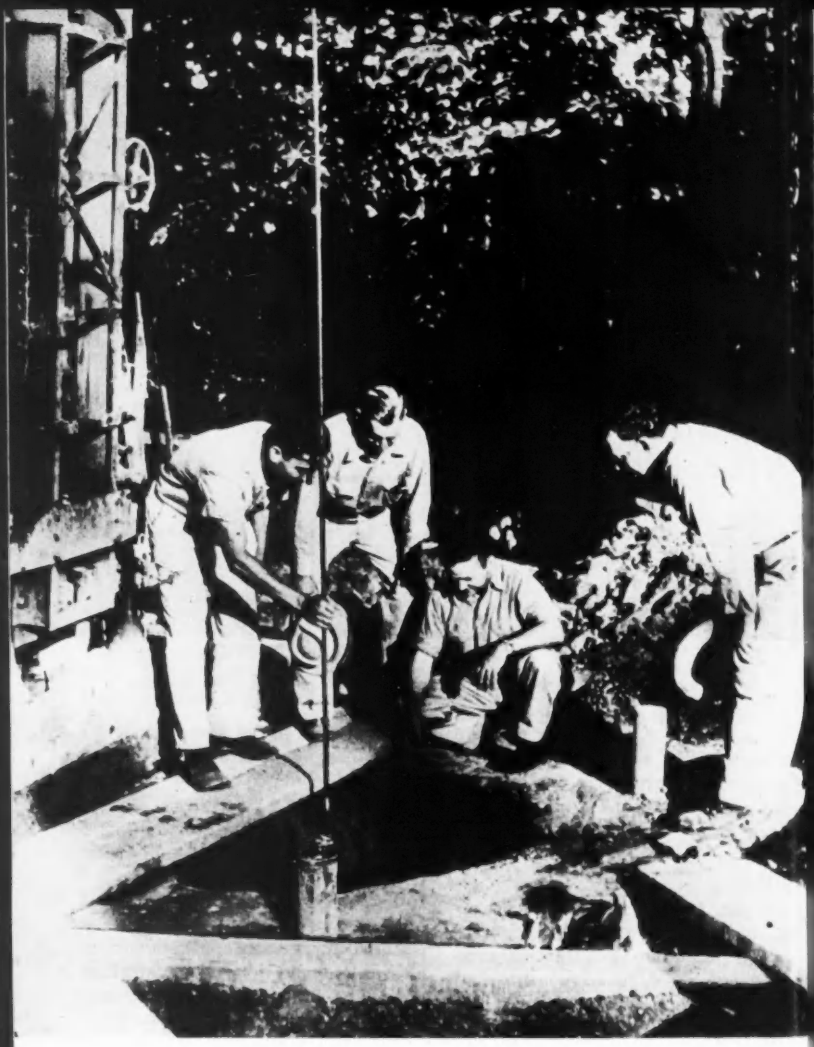
➤ OFFICIALS *plan to convert the coal in this Alabama seam to fuel gas.*

due to leakage of gas and air pressure through cracks and breaks in the 30-foot layer of earth over the burning seam. A leakage is not expected in the second trial because the 40-inch seam to be burned is 100 feet below the surface.

In the 1947 experiment, not only air under pressure was used to support the combustion. Various mixtures were tested. An oxygen-enriched air blast gave excellent results, as did also oxygen-steam-air blasts and oxygen-steam blasts. All will be tried again in the new trial. It is thought that better-quality products will be obtained with the use of oxygen and steam.

To many it might seem that if the coal underground is actually burned, the gases obtained would have no value for heating and power. If complete combustion occurred this might be true, by complete meaning what takes place in a properly managed furnace where both solids and gases are consumed. Plenty of oxygen is essential for complete combustion. Otherwise gases formed, or distilled out of the coal by the heat, are burnable.

In the manufacture of coke from bituminous coal great volumes of combustible gas are obtained as a by-product, and this gas has high heating value. The carbon monoxide from the



➤ A LARGE *bore-hole sunk to the coal seam in the coal-burning experiment at Gorgas, Alabama. This is the second experiment on getting fuel gas by controlled burning of underground coal conducted by the Alabama Power Co. and the U. S. Bureau of Mines.*

household stove, responsible for many deaths, is a combustible gas from the coal, a result of incomplete combustion.

Manufactured gas, widely used in America in locations in which natural gas is not available, is another example of gas from coal. Two kinds are used, coal gas and water gas, but both are made from coal. In the first, coal is heated in retorts in the absence of air. The so-called water gas is made by passing steam through coke that has been heated white hot. A chemical action takes place, which produces a mixture of carbon monoxide and hydrogen. Coal gas is largely methane and hydrogen. Natural gas is largely methane.

In the Alabama underground coal-burning experiment the combustion is under control. Cutting its supply of oxygen extinguishes it. However, there are many underground coal fires that are not under control. They may be called accidental fires, man-made but through carelessness. They originated at coal outcrops from bush fires, or in abandoned mines from burning debris. Many have been burning for years. Air enough to supply oxygen for combustion keeps them alive. No attempts have been made to capture and harness the gases given off, but it may be tried when the Alabama experiments are completed.

Underground fuel without mining is being obtained in Sweden in an experiment paralleling the Alabama undertaking, but it is from heat, not fire. Electrical heaters, in deep drill holes into layers of oil shale, are distilling the oil from the shale, permitting it to escape in gaseous form to the surface for capture, refinement and use.

The electrical resistance heaters dropped into the holes require some three months to warm up the oil shale. This is followed by a two-month oil vapor production period. The process is pronounced by American scientists to be feasible here but too costly. Sweden has cheap hydro-electric energy close to its oil shale deposits. Underground coal-burning is an easy process.

Fuel Oils from Coal

➤CHEAPER GASOLINE and fuel oil from coal is promised by improved processes under development at the U. S. Bureau of Mines experimental and research laboratories in Bruceton, Pa., near Pittsburgh.

In these laboratories, a basically new approach to the problem of synthetic liquid fuel production by direct hydrogenation of coal is under investigation, the American Chemical Society was told recently by Dr. Henry H. Storch, chief of research at the institution. The method, he said, is a departure from the conventional Bergius process used by the Germans.

In this German process, coal dust is mixed with oil to form a paste. This is then treated with hot hydrogen under a pressure of more than 2,000 pounds per square inch. In the new process, Bureau chemists are trying to achieve better results by using moderate pressures and relatively high temperatures. Under these conditions considerable coal is turned to coke, but the coke can be recovered and used to furnish heat for the process.

In the new developments, relatively inexpensive water gas may replace

the expensive hydrogen. The cost of compressed hydrogen constitutes about 50% of the total cost of liquid fuels prepared by hydrogenation of coal. Water gas, made by passing steam over white-hot coke, is the common manufactured gas used in many cities where natural gas is not available.

Laboratory experiments have disclosed that under appropriate operating conditions it is possible to replace pure hydrogen with the water gas, which is itself a mixture of hydrogen and carbon monoxide. Similarly, it is also possible to substitute for pure hydrogen the light, gaseous by-products of the hydrogenation process. Coal itself contains some available hydrogen which can be exploited by converting the coal to coke.

An entirely different process is also under study. In this the coal is dissolved before being treated with hydrogen. Research is now directed at determining the best solvent, and also at discovering suitable catalysts to speed the hydrogenation action under these conditions. This process is carried out at relatively low temperatures and pressures.

Rare Elements Now Useful

➤ RARE CHEMICAL elements, some of which were recently thought to be useless, are finding an increasing number of important applications in science and industry today, according to Dr. Dallas T. Hurd, General Electric Research Laboratory chemist.

Citing as an example uranium, Dr. Hurd said in the WGY broadcast that a decade ago this element was used commercially "only in small amounts for a few odd jobs such as coloring of glass and china." Since then uranium has become of paramount importance in the development of atomic energy.

Polonium, a radioactive element so rare that the quantities used can hardly be weighed and are invisible to the naked eye, is now used to dissipate potentially-dangerous static electricity, he stated. Radiations from polonium, harmless to humans, turn the surrounding air into an electrical conductor, and the static leaks off as it is formed. Easily plated on other metals, polonium can be used effectively in small quantities.

Crystals of germanium, an element which sits on the chemical borderline between metals and insulators, are expected by some radio engineers to replace vacuum tubes in future radio sets. Dr. Hurd predicted that smaller, lighter radios, graduating toward the two-way wrist radio of Dick Tracy, will result.

These tiny crystals act as rectifiers, that is, they change alternating current to direct current. This property of germanium made the element "extremely important in radar work during the war . . . ," and applications have been found in the high-frequency radio work common today in television, FM, and commercial radar.

Another of the rare elements described by Dr. Hurd is indium. Now used in corrosion-resistant bearings, indium was once displayed as a metal for which there is no use.

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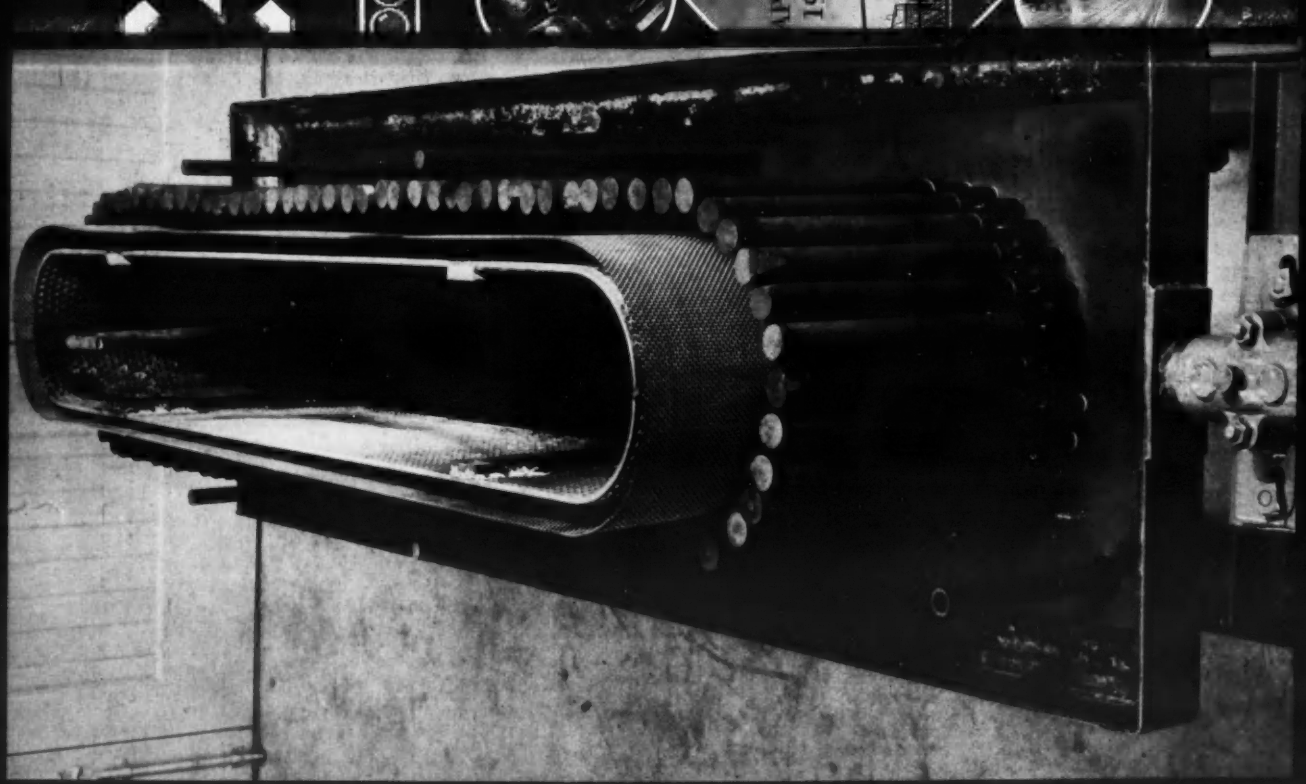
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